Supporting Information

Site-Selective Catalysis of Phenyl Thionoformate Transfer as a Tool for Regioselective Deoxygenation of Polyols

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1. General Procedures:

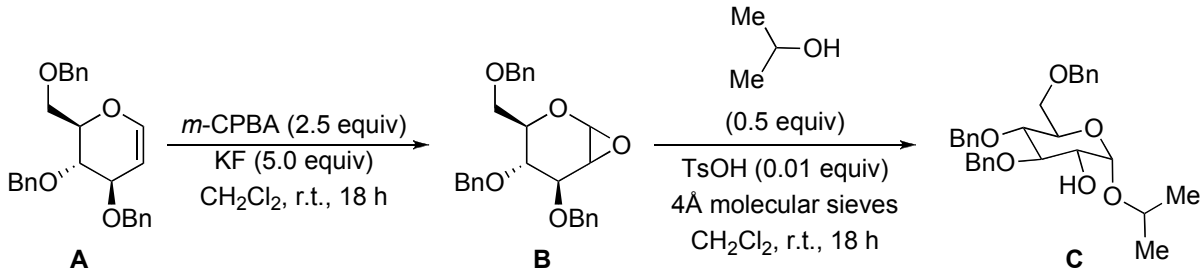
Proton NMR spectra were recorded on a 400 or 500 MHz spectrometer. Proton chemical shifts were reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00 ppm) or with the solvent reference relative to TMS employed as the internal standard ($CDCl_3$, δ 7.26 ppm; CD_3OD, δ 3.31 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublets of doublets (ddd), doublet of triplets (dt), doublet of quartets (dq), triplet (t), quartet (q), and multiplet (m)], coupling constants [Hz], integration). Carbon NMR spectra were recorded on a 500 (125) MHz spectrometer with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to the residual solvent signal ($CDCl_3$, δ 77.0 ppm; CD_3OD, δ 49.2 ppm). All NMR spectra were acquired at ambient temperature. Infrared spectra were obtained on a FT-IR spectrometer, υ_{max} (cm^{-1}) and are partially reported. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 pre-coated plates (0.25 mm thickness). TLC R_f values are reported. Visualization was accomplished by irradiation with a UV lamp and/or staining with cerium ammonium molybdate (CAM) or $KMnO_4$ solutions. Flash column chromatography was performed using Silica Gel 60 Å (32-63 μm). High resolution mass spectra were acquired by the method of ionization is indicated in parentheses.

All reactions were carried out under a nitrogen atmosphere employing oven- and/or flame-dried glassware. Solvents were purified using a Solvent Purification System. *N*-methylimidazole and pyridine were distilled and stored in a Schlenk flask prior to use. 2,4,6-Tribenzyl *myo*-inositol (**10**) was prepared in three steps from commercially available *myo*-inositol according to the method of Billington and coworkers.[1] Glucosamine derivative **11** was prepared in four steps from commercially available *N*-acetyl-D-glucosamine following the procedure of RajanBabu and coworkers.[2] α- and β-methyl glucosides **12a** and **32** were prepared in one step from α– or β-D-glucose according to the procedure of Stick and coworkers.[3] Peptide **27**[4] and **28**[5] were prepared according to standard solid phase peptide coupling procedures. All other chemicals were purchased commercially and used as received.

2. Experimental Procedures:

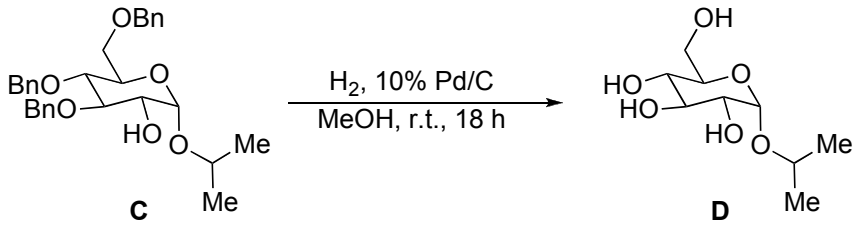
2.1 Preparation of Substrates for Thiocarbonylation:

Intermediate C.



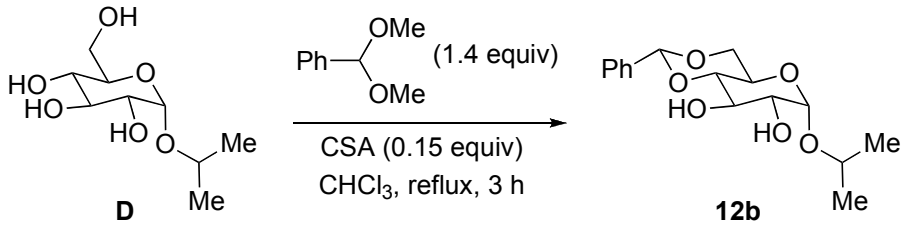
Compound **B** was synthesized according to previously reported methods.[6] Epoxide **B** (650 mg, 1.50 mmol) was suspended in CH_2Cl_2 (11.0 mL) and 4Å molecular sieves were added. Then, 2-propanol (57 μL, 0.75 mmol) and p-toluenesulfonic acid (3.0 mg, 0.015 mmol) were added and the mixture was allowed to stir overnight (18 h) at room temperature. The mixture was then concentrated under reduced pressure and purified through silica gel flash chromatography (4:1, hexanes:EtOAc) to yield the α-anomer **C** (146 mg, 20 %) and the β-anomer (296 mg, 40 %), both as white solids. The spectral data for compound **C** matched that which had been previously reported.[7]

Intermediate D.



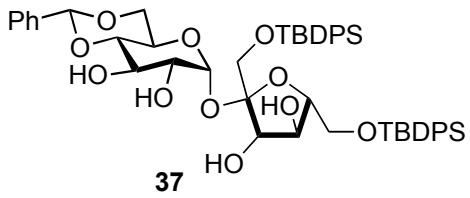
Palladium on carbon (10%, 100 mg) was added to an N_2 flushed suspension of tribenzoate **C** (140 mg, 0.28 mmol) in methanol (3.0 mL) and the mixture was then allowed to stir under an atmosphere of H_2 at room temperature overnight (18 h). The mixture was then filtered through celite, washed with CH_2Cl_2, and concentrated under reduced pressure. Purification through silica gel flash chromatography (5:1 dichloromethane:methanol) afforded **D** as a white solid (48 mg, 77%). The spectral data for compound **D** matched that which had been previously reported.[8]

4, 6-*O*-Benzylidene α- isopropyl glucoside 12b.



Compound **12b** was synthesized through modified procedure of Stick and coworkers.[3] Benzaldehyde dimethyl acetal (65.0 mL, 0.434 mmol) and camphor sulfonic acid (13.0 mg, 0.047 mmol) were added to a suspension of glucose derivative **D** (70 mg, 0.31 mmol) in $CHCl_3$ (2.0 mL). After the mixture was stirred at reflux for 2.5 h, a distillation apparatus was attached to the round bottom flask to remove the methanol generated. When most of the $CHCl_3$-MeOH solvent mixture was distilled off, more $CHCl_3$ was added (3x) and distilled to insure all methanol was removed. Upon cooling, the mixture was washed with saturated $NaHCO_3$, water, and dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification through silica gel flash chromatography (10:1, dichloromethane:methanol) afforded **12b** as a white solid (64.0 mg, 67%). Data for **12b: mp** 53-57°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.52-7.50 (m, 2H), 7.39-7.36 (m, 3H), 5.54 (s, 1H), 4.99 (d, *J* = 4.1 Hz, 1H), 4.27 (dd, *J* = 4.9, 10.2 Hz, 1H), 3.98-3.86 (m, 3H), 3.73 (t, *J* = 10.4 Hz, 1H), 3.59 (dd, *J* = 4.1, 9.1 Hz, 1H), 3.50 (t, *J* = 9.9 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.21 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 137.0, 129.1, 128.2, 126.2, 101.7, 97.2, 80.9, 72.6, 71.7, 70.8, 68.8, 62.4, 23.3, 21.6; **IR** (film, cm^{-1}) 3391, 2970, 2921, 1380, 1069, 1029; **TLC** R_f 0.36 (10:1 dichloromethane-methanol); **$[\alpha]_D^{20.0}$** -11.6 (*c* 0.84, $CHCl_3$); **HRMS** calcd for $[C_{16}H_{22}O_6\ Na]^+$ requires *m/z* 333.1314; found 333.1327 (ESI+).

4, 6-*O*-benzylidene-1′, 6′-bis-*O*- *t*-butyldiphenylsilyl sucrose 37.



This compound was prepared via a combination of the procedures reported by Montesarchio and coworkers and Khan and coworkers.[9] Sucrose (300 mg, 0.88 mmol) was suspended in pyridine (3 mL) and heated to 90 °C in a flame dried 500 mL round bottom flask. Then benzal bromide (0.30 mL, 0.88 mmol) was added in two aliquots over a 2 hour period and the

reaction mixture was allowed to stir for another 2 hours. Upon cooling of the brown suspension to room temperature, t-butyldiphenylsilyl chloride (0.45 mL, 1.76 mmol) and 4-dimethylaminopyridine (9.0 mg, 0.07 mmol) were added and the mixture was allowed to stir overnight. The mixture was then concentrated under reduced pressure and purified by silica gel flash chromatography (20:1, dichloromethane-methanol) to yield a white solid (162 mg, 20%). Data for **37: mp** 54-58°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.74-7.67 (m, 9H), 7.48-7.34 (m, 16H), 5.50 (d, *J* = 4.1 Hz, 1H), 5.49 (s, 1H), 4.13 (br s, 2H), 4.02 (dd, *J* = 4.9, 10.0 Hz, 1H), 3.92 (dt, *J* = 5.0, 10.0 Hz, 1H), 3.88-3.83 (m, 4H), 3.80 (d, *J* = 11.0 Hz, 1H), 3.69 (d, *J* = 11.0 Hz, 1H), 3.56 (t, *J* = 10.2 Hz, 1H), 3.45-3.38 (m, 2H), 2.96 (br s, 2H), 2.44 (br s, 1H), 2.36 (br s, 1H), 1.08 (m, 18H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 136.9, 135.7, 135.6, 135.5, 135.2, 134.8, 133.0, 132.8, 132.4, 130.0, 130.0, 129.9, 129.8, 129.6, 129.2, 128.3, 127.9, 127.8, 127.7, 126.3, 104.6, 101.8, 92.0, 80.8, 80.5, 78.7, 76.4, 72.3, 71.5, 68.5, 65.4, 64.2, 63.4, 26.9, 26.8, 26.5, 19.2, 19.1, 19.0; **IR** (film, cm^{-1}) 3415, 2929, 2851, 1429, 1114, 1069, 706; **TLC** R_f 0.30 (10:1 dichloromethane-methanol); **$[\alpha]_D^{20.0}$** +14.0 (*c* 0.97, $CHCl_3$); **HRMS** calcd for $[C_{51}H_{62}O_{11}Si_2\ Na]^+$ requires *m/z* 929.3728; found 929.3715 (ESI+).

2.2 General Procedures for the Thiocarbonylation Reaction:

General Procedure A

Phenyl chlorothionoformate (1.5 equiv), 1,2,2,6,6-pentamethyl piperidine (2.0 equiv), and *N*-methylimidazole or a peptide catalyst (0.20 equiv) were added sequentially to a flame dried 10 mL round bottom flask containing a solution of alcohol, diol, or polyol (1.0 equiv) in anhydrous dichloromethane (1 mL). The reaction (yellow or brown) solution was stirred at room temperature for 1 hour, then quenched with 1 mL of methanol and concentrated under reduced pressure. The mixture of reaction products was isolated by silica gel flash chromatography.

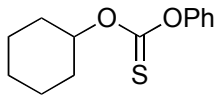
General Procedure B

Phenyl chlorothionoformate (1.5 equiv), 1,2,2,6,6-pentamethyl piperidine (2.0 equiv), *N*-methylimidazole or a peptide catalyst (0.20 equiv), and $FeCl_3$ (0.15 equiv) were added sequentially to a flame dried 10 mL round bottom flask containing a solution of alcohol, diol, or polyol (1.0 equiv) in anhydrous dichloromethane (1 mL). The reaction (yellow or brown) mixture was stirred at room temperature for 1 hour, then quenched with 1 mL of methanol

and concentrated under reduced pressure. The mixture of reaction products was isolated by silica gel flash chromatography.

NOTE: Optimized reaction conditions are described for each respective substrate. Unless otherwise noted, reactions were run according to conditions (General Procedure A or B) described above.

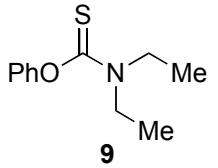
Compound 8.



8

General procedure B for thiocarbonylation was followed, cyclohexanol (21.0 μL, 0.20 mmol) was employed as starting material with *N*-methylimidazole (3.0 μL, 0.04 mmol), phenyl chlorothionoformate (140.0 μL, 1.0 mmol), 1,2,2,6,6-pentamethyl piperidine (72.0 μL, 0.40 mmol), and $FeCl_3$ (16.0 mg, 0.10 mmol), in CH_2Cl_2 (2.0 mL). Purification through a short plug of silica gel (dichloromethane) afforded an inseparable 2.4:1 mixture of **8**:**25** as a colorless oil (57 mg, 60%). Data for **8**: **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.35-7.32 (m, 2H), 7.22-7.18 (m, 1H), 7.04-7.02 (m, 2H), 5.20-5.15 (m, 1H), 2.01-1.98 (m, 2H), 1.72-1.68 (m, 2H), 1.61-1.46 (m, 3H), 1.39-1.32 (m, 2H), 1.28-1.24 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 194.2, 153.3, 129.4, 126.4, 122.0, 83.4, 30.8, 25.2, 23.5; **IR** (film, cm^{-1}) 2942, 2856, 1491, 1287, 1197, 1017, 772, 686; **TLC** R_f 0.50 (10:1 hexanes-EtOAc); **HRMS** calcd for $[C_{13}H_{17}O_2S\ H]^+$ requires *m/z* 237.0949; found 237.0959 (ESI+).

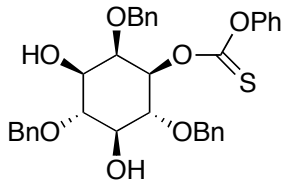
Compound 9.



9

The spectral data for compound **9** matched that which had been previously reported.[10]

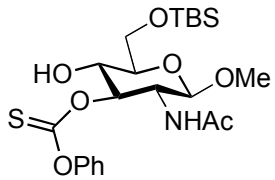
Compound (±)-13.



(±)-13

General procedure A for thiocarbonylation was followed, 2,4,6-tribenzyl *myo*-inositol **10** (100 mg, 0.22 mmol) was employed as starting material with *N*-methylimidazole (3.50 μL, 0.044 mmol), phenyl chlorothionoformate (45.0 μL, 0.33 mmol), and 1,2,2,6,6-pentamethyl piperidine (79.5 μL, 0.44 mmol) in CH_2Cl_2 (5 mL). Purification through silica gel flash chromatography (7:1 to 4:1 hexanes-EtOAc) afforded (±)-**13** as a colorless oil (101 mg, 78%). Data for (±)-**13:** **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.42-7.30 (m, 18H), 7.03-7.02 (m, 2H), 5.34 (dd, *J* = 2.5, 10.1 Hz, 1H), 4.95 (d, *J* = 11.4 Hz, 1H), 4.90-4.79 (m, 6H), 4.43 (t, *J* = 2.5 Hz, 1H), 4.13 (t, *J* = 9.6 Hz, 1H), 3.79 (t, *J* = 9.5 Hz, 1H), 3.69-3.66 (m, 2H), 2.56 (br s, 1H), 2.32 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 194.2, 153.3, 138.5, 138.3, 138.1, 129.6, 128.6, 128.5, 128.5, 128.0, 128.0, 127.9, 127.9, 127.8, 126.7, 121.8, 83.8, 81.2, 79.5, 76.4, 75.3, 75.0, 74.8, 71.8; **IR** (film, cm^{-1}) 3559, 3452, 3056, 3031, 2911, 2873, 1488, 1451, 1281, 1199, 1017, 734, 696; **TLC** R_f 0.52 (2:1 hexanes-EtOAc); **HRMS** calcd for $[C_{34}H_{35}O_7S\ H]^+$ requires *m/z* 587.2104; found 587.2108 (ESI+).

Glucosamine 3-mono(thiocarbonate) 20.

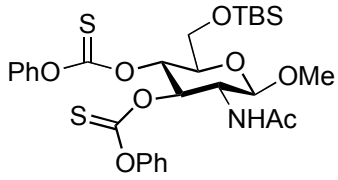


20

General procedure A for thiocarbonylation was followed, glucosamine derivative **11** (58 mg, 0.17 mmol) was employed as starting material with *N*-methylimidazole (2.71 μL, 0.034 mmol), phenyl chlorothionoformate (34.5 μL, 0.255 mmol), and 1,2,2,6,6-pentamethyl piperidine (61.5 μL, 0.34 mmol) in CH_2Cl_2 (3 mL). Purification through silica gel flash chromatography (2:1 to 1:1 hexanes-EtOAc) afforded a 3:1 mixture of **20:21** as a white solid (60 mg, 67%). Data for **20**: **mp** 155-158°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.42-7.39 (m, 2H), 7.31-7.28 (m, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 5.75 (dd, *J* = 8.8, 10.7 Hz, 1H); 5.69 (d, *J* =

9.1 Hz, 1H), 4.54 (d, *J* = 8.2 Hz, 1H); 4.08 (dd, *J* = 8.2, 10.7 Hz, 1H); 4.04-4.00 (m, 1H), 3.96 (t, *J* = 9.1 Hz, 1H); 3.88 (dd, *J* = 6.3, 10.4 Hz, 1H), 3.53-3.49 (m, 1H), 3.49 (s, 3H), 1.99 (s, 3H), 1.66 (br s, 1H), 0.91 (s, 9H), 0.12 (d, *J* = 3.8, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 196.6, 170.2, 153.4, 129.5, 126.7, 121.7, 101.7, 84.9, 73.8, 71.9, 64.7, 56.5, 54.4, 25.8, 23.6, 18.2, -5.4, -5.5; **IR** (film, cm^{-1}) 3277, 2929, 2852, 1659, 1487, 1287, 1205, 1046, 841, 686; **TLC** R_f 0.26 (10:1 dichloromethane-EtOAc); **$[\alpha]_D^{20.0}$** -71.5 (*c* 0.87, $CHCl_3$); **HRMS** calcd for $[C_{22}H_{36}NO_7SSi\ H]^+$ requires *m/z* 486.1982; found 486.2000 (ESI+).

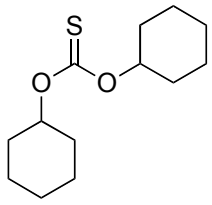
Glucosamine 3,4-bis(thiocarbonate) 21.



21

Data for **21: mp** 152-157°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.42-7.39 (m, 4H), 7.32-7.29 (m, 2H), 7.06-7.03 (m, 4H), 6.27 (dd, *J* = 8.7, 10.2 Hz, 1H), 5.84 (t, *J* = 9.1 Hz, 1H), 5.76 (d, *J* = 8.2 Hz, 1H), 4.88 (d, *J* = 8.2 Hz, 1H), 3.94-3.80 (m, 4H), 3.54 (s, 3H), 2.02 (s, 3H), 0.91 (s, 9H), 0.10 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.4, 193.8, 170.3, 153.5, 153.4, 129.5, 126.8, 126.7, 121.9, 121.8, 100.8, 82.1, 78.0, 74.2, 62.1, 56.7, 55.3, 25.9, 23.6, 18.3, -5.2, -5.3; **IR** (film, cm^{-1}) 3293, 3097, 2929, 2852, 1659, 1487, 1287, 1205, 1078, 850, 768; **TLC** R_f 0.40 (10:1 dichloromethane-EtOAc); **$[\alpha]_D^{20.0}$** +52.3 (*c* 0.34, $CHCl_3$); **HRMS** calcd for $[C_{29}H_{40}NO_8S_2Si\ H]^+$ requires *m/z* 622.1965; found 622.1982 (ESI+).

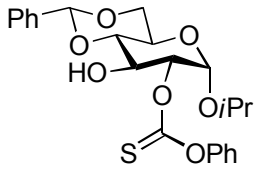
Compound 25.



25

The spectral data for compound **25** matched that which had been previously reported.[11]

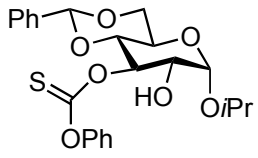
4, 6-*O*-Benzylidene 2-mono(thiocarbonate) α-isopropyl glucoside 22b.



22b

General procedure A for thiocarbonylation was followed, glucose derivative **12b** (10 mg, 0.03 mmol) was employed as starting material with peptide **27** (5.4 mg, 0.006 mmol), phenyl chlorothionoformate (6.0 μL, 0.045 mmol), and 1,2,2,6,6-pentamethyl piperidine (11 μL, 0.06 mmol), in CH_2Cl_2 (0.5 mL). Percent conversion, as determined by crude ^{1}H NMR, showed a 7.4:1 product ratio of **22b**:**23b** (**12b** 3%; **22b** 59%; **23b** 8%; **24b** 22%; **26b** 8%). Data for **22b**: **mp** 120-122°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.55-7.30 (m, 8H), 7.13-7.11 (m, 2H), 5.59 (s, 1H), 5.52 (d, *J* = 3.8 Hz, 1H), 5.22 (dd, *J* = 3.8, 9.5 Hz, 1H), 4.42 (t, *J* = 9.6 Hz, 1H), 4.32 (dd, *J* = 5.0, 10.4 Hz, 1H), 4.04 (dt, *J* = 4.8, 10.1 Hz, 1H), 3.94 (m, *J* = 6.3 Hz, 1H), 3.78 (t, *J* = 10.4 Hz, 1H), 3.64 (t, *J* = 9.5 Hz, 1H), 2.62 (br s, 1H), 1.30 (d, *J* = 6.3 Hz, 3H), 1.23 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 194.6, 153.3, 136.9, 129.6, 129.3, 128.4, 126.7, 126.3, 121.8, 102.1, 93.7, 81.8, 81.3, 71.3, 68.9, 68.8, 62.2, 23.3, 21.7; **IR** (film, cm^{-1}) 3465, 2974, 2921, 1491, 1340, 1275, 1205, 1062, 1033; **TLC** R_f 0.55 (2:1 hexanes-EtOAc); **[α]** $^{20.0}_{D}$ +93 (*c* 0.60, $CHCl_3$); **HRMS** calcd for $[C_{23}H_{27}O_7S\ H]^+$ requires *m/z* 447.1478; found 447.1483 (ESI+).

4, 6-*O*-Benzylidene 3-mono(thiocarbonate) α- isopropyl glucoside 23b.

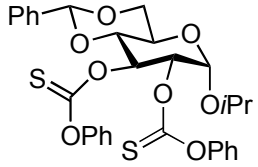


23b

General procedure B for thiocarbonylation was followed, glucose derivative **12b** (9.0 mg, 0.029 mmol) was employed as starting material with peptide **28** (8.3 mg, 0.006 mmol), phenyl chlorothionoformate (6.0 μL, 0.044 mmol), 1,2,2,6,6-pentamethyl piperidine (10.5 μL, 0.058 mmol), and $FeCl_3$ (0.7 mg, 0.004 mmol), in CH_2Cl_2 (0.4 mL). Percent conversion, as determined by crude ^{1}H NMR, showed a 1:3 product ratio of **22b**:**23b** (**12b** 40%; **22b** 13%; **23b** 36%; **24b** 0%; **26b** 11%). Data for **23b**: **mp** 53-56°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.41-7.39 (m, 2H), 7.30-7.27 (m, 5H), 7.19-7.15 (m, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 5.84 (t, *J*

= 9.5 Hz, 1H), 5.45 (s, 1H), 4.96 (d, *J* = 3.8 Hz, 1H), 4.21 (dd, *J* = 4.7, 10.4 Hz, 1H), 3.95-3.86 (m, 2H), 3.80-3.76 (m, 1H), 3.70-3.65 (m, 2H), 2.13 (d, *J* = 12.0 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.7, 153.5, 136.9, 129.4, 129.0, 128.2, 126.5, 126.1, 121.9, 101.4, 97.6, 82.4, 78.8, 71.5, 68.8, 62.7, 23.3, 21.7; **IR** (film, cm^{-1}) 3469, 2970, 2929, 1491, 1287, 1201, 1070, 1033; **TLC** R_f 0.40 (2:1 hexanes-EtOAc); **[α]** $^{20.0}_{D}$ -8.5 (*c* 1.0, $CHCl_3$); **HRMS** calcd for $[C_{23}H_{27}O_7S\ H]^+$ requires *m/z* 447.1478; found 447.1470 (ESI+).

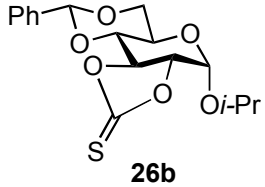
4, 6-*O*-Benzylidene 2,3-bis(thiocarbonate) α- isopropyl glucoside 24b.



24b

Data for **24b**: **mp** 64-68°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.53-7.29 (m, 11H), 7.13-7.05 (m, 4H), 6.30 (t, *J* = 9.5 Hz, 1H), 5.61 (s, 1H), 5.56 (d, *J* = 3.8 Hz, 1H), 5.54 (dd, *J* = 4.1, 9.5 Hz, 1H), 4.36 (dd, *J* = 5.0, 10.4 Hz, 1H), 4.18 (dt, *J* = 4.7, 10.1 Hz, 1H), 3.97 (m, *J* = 6.1 Hz, 1H), 3.92 (t, *J* = 9.8 Hz, 1H), 3.84 (t, *J* = 10.4 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 194.2, 194.1, 153.6, 153.3, 136.8, 129.6, 129.5, 129.1, 128.3, 126.8, 126.6, 126.2, 121.9, 121.7, 101.6, 94.1, 79.5, 79.4, 78.6, 71.6, 68.8, 62.4, 23.2, 21.6; **IR** (film, cm^{-1}) 2974, 2921, 1487, 1454, 1275, 1225, 1193; **TLC** R_f 0.63 (2:1 hexanes-EtOAc); **[α]** $^{20.0}_{D}$ -33.0 (*c* 0.49, $CHCl_3$); **HRMS** calcd for $[C_{30}H_{31}O_8S_2\ H]^+$ requires *m/z* 583.1460; found 583.1442 (ESI+).

Compound 26b.

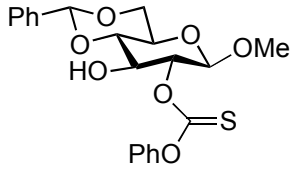


26b

Data for **26b**: **mp** 69-72°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.51-7.49 (m, 2H), 7.41-7.38 (m, 3H), 5.62 (s, 1H), 5.44 (d, *J* = 3.2 Hz, 1H), 4.98 (dd, *J* = 9.9, 12.1 Hz, 1H), 4.33-4.30 (m, 1H), 4.30 (dd, *J* = 3.2, 12.0 Hz, 1H), 4.11 (dd, *J* = 8.5, 10.1 Hz, 1H), 4.03 (m, *J* = 6.0 Hz,

1H), 3.90 (t, *J* = 9.9 Hz, 1H), 3.88-3.83 (m, 1H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.25 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 190.5, 136.2, 129.3, 128.3, 126.0, 101.3, 94.5, 80.5, 80.1, 79.2, 72.6, 68.4, 64.8, 23.2, 21.4; **IR** (film, cm^{-1}) 2974, 1381, 1291, 1099, 1029; **TLC** R_f 0.45 (2:1 hexanes-EtOAc); **[α]** $^{20.0}_{D}$ -78.0 (*c* 0.59, $CHCl_3$); **HRMS** calcd for $[C_{17}H_{21}O_6S\ H]^+$ requires *m/z* 353.1059; found 353.1064 (ESI+).

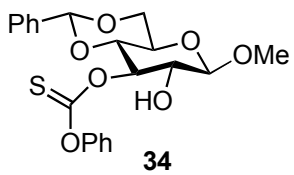
4, 6-*O*-Benzylidene 2-mono(thiocarbonate) β-methyl glucoside 33.



33

General procedure A for thiocarbonylation was followed, glucose derivative **32** (10 mg, 0.035 mmol) was employed as starting material with peptide **28** (10 mg, 0.007 mmol), phenyl chlorothionoformate (7.0 μL, 0.053 mmol), and 1,2,2,6,6-pentamethyl piperidine (13 μL, 0.07 mmol), in CH_2Cl_2 (0.5 mL). Percent conversion, as determined by crude ^{1}H NMR, showed a 1.5:1 product ratio of **33**:**34** (**32** 7%; **33** 14%; **34** 10%; **35** 36%; **36** 33%). Data for **33**: **mp** 175-178°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.52-7.51 (m, 2H), 7.45-7.39 (m, 5H), 7.33-7.30 (m, 1H), 7.18-7.16 (m, 2H), 5.60 (t, *J* = 8.4 Hz, 1H), 5.58 (s, 1H), 4.63 (d, *J* = 7.9 Hz, 1H), 4.42 (dd, *J* = 5.0, 10.4 Hz, 1H), 4.15-4.10 (m, 1H), 3.83 (t, *J* = 10.2 Hz, 1H), 3.70 (t, *J* = 9.5 Hz, 1H), 3.60 (s, 3H), 3.55-3.51 (m, 1H), 2.67 (d, *J* = 3.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.1, 153.5, 136.8, 129.5, 129.0, 128.4, 126.7, 126.3, 121.8, 102.0, 82.8, 81.8, 80.7, 72.5, 68.7, 66.2, 57.4; **IR** (film, cm^{-1}) 3481, 2971, 1283, 1205, 1091, 1001; **TLC** R_f 0.35 (2:1 hexanes-EtOAc); **[α]** $^{20.0}_{D}$ -58.1 (*c* 1.0, $CHCl_3$); **HRMS** calcd for $[C_{21}H_{23}O_7S\ H]^+$ requires *m/z* 419.1165; found 419.1159 (ESI+).

4, 6-*O*-Benzylidene 3-mono(thiocarbonate) β-methyl glucoside 34.

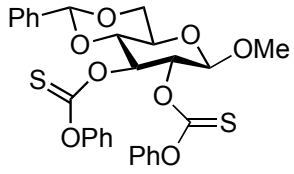


34

General procedure A for thiocarbonylation was followed, glucose derivative **32** (10 mg, 0.035 mmol) was employed as starting material with peptide **27** (6.3 mg, 0.007 mmol),

phenyl chlorothionoformate (7.0 μL, 0.053 mmol), and 1,2,2,6,6-pentamethyl piperidine (13 μL, 0.07 mmol), in CH_2Cl_2 (0.5 mL). Percent conversion, as determined by crude ^{1}H NMR, showed a 1:1.5 product ratio of **33**:**34** (**32** 0%; **33** 18%; **34** 27%; **35** 25%; **36** 30%). Data for **34: mp** 68-72°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.51-7.28 (m, 8H), 7.10 (d, *J* = 7.6 Hz, 2H), 5.89 (t, *J* = 9.5 Hz, 1H), 5.57 (s, 1H), 4.48 (d, *J* = 7.6 Hz, 1H), 4.43 (dd, *J* = 4.9, 10.8 Hz, 1H), 3.88-3.81 (m, 3H), 3.64-3.59 (m, 4H), 2.62 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.3, 153.5, 136.8, 129.5, 129.1, 128.2, 126.6, 126.1, 121.8, 104.3, 101.5, 82.7, 78.6, 73.3, 68.6, 66.2, 57.7; **IR** (film, cm^{-1}) 3463, 2941, 2874, 1496, 1278, 1200, 1089, 1074, 1030, 1000, 696; **TLC** R_f 0.18 (2:1 hexanes-EtOAc); **$[\alpha]_D^{20.0}$** -21.5 (*c* 0.69, $CHCl_3$); **HRMS** calcd for $[C_{21}H_{23}O_7S\ H]^+$ requires *m/z* 419.1165; found 419.1177 (ESI+).

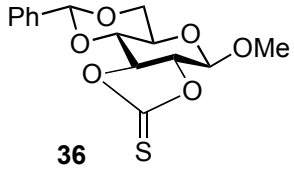
4, 6-*O*-Benzylidene 2,3-bis(thiocarbonate) β-methyl glucoside 35.



35

Data for **35: mp** 73-78°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.52-7.29 (m, 11H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.13 (dd, *J* = 8.5, 9.5 Hz, 1H), 5.84 (dd, *J* = 7.7, 8.3 Hz, 1H), 5.60 (s, 1H), 4.79 (d, *J* = 7.6 Hz, 1H), 4.47 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.05 (t, *J* = 9.5 Hz, 1H), 3.89 (t, *J* = 10.4 Hz, 1H), 3.69 (dt, *J* = 4.8, 9.9 Hz, 1H), 3.63 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 194.7, 194.4, 153.6, 153.5, 136.7, 129.5, 129.4, 129.2, 128.3, 126.8, 126.7, 126.2, 122.0, 121.9, 101.7, 101.6, 81.4, 81.3, 78.0, 68.6, 66.0, 57.5; **IR** (film, cm^{-1}) 2933, 1485, 1289, 1204, 1096, 1063, 689; **TLC** R_f 0.40 (2:1 hexanes-EtOAc); **$[\alpha]_D^{20.0}$** -92.9 (*c* 0.68, $CHCl_3$); **HRMS** calcd for $[C_{28}H_{27}O_8S_2\ H]^+$ requires *m/z* 555.1147; found 555.1160 (ESI+).

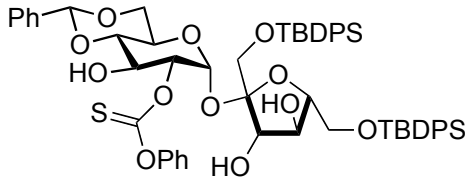
Compound 36.



36

Data for **36: mp** 147-150°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.50-7.48 (m, 2H), 7.40-7.38 (m, 3H), 5.62 (s, 1H), 4.87 (d, *J* = 7.9 Hz, 1H), 4.53 (dd, *J* = 9.8, 12.0 Hz, 1H), 4.42 (dd, *J* = 4.7, 10.8 Hz, 1H), 4.14 (dd, *J* = 7.9, 12.0 Hz, 1H), 4.11 (dd, *J* = 8.7, 10.3 Hz, 1H), 3.95 (t, *J* = 10.4 Hz, 1H), 3.62 (s, 3H), 3.54-3.51 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 189.9, 136.0, 129.4, 128.4, 126.0, 101.4, 101.3, 81.8, 81.2, 78.6, 69.1, 68.2, 57.3; **IR** (film, cm^{-1}) 2921, 1456, 1296, 1276, 1096, 1004, 968; **TLC** R_f 0.35 (2:1 hexanes-EtOAc); **$[\alpha]_D^{20.0}$** -97.5 (*c* 1.0, $CHCl_3$); **HRMS** calcd for $[C_{15}H_{17}O_6S\ H]^+$ requires *m/z* 325.0746; found 325.0735 (ESI+).

4,6-*O*-benzylidene-1´,6´-bis-*O*- t-butyldiphenylsilyl 2-mono(thiocarbonate) sucrose 38.

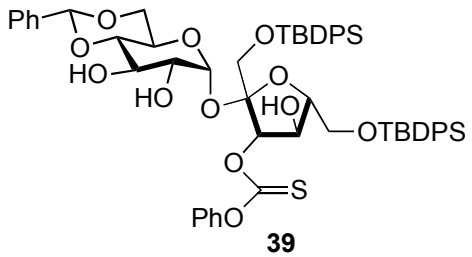


38

General procedure A for thiocarbonylation was followed, sucrose derivative **37** (49 mg, 0.054 mmol) was employed as starting material with peptide **27** (10 mg, 0.011 mmol), phenyl chlorothionoformate (11 μL, 0.081 mmol), and 1,2,2,6,6-pentamethyl piperidine (20 μL, 0.108 mmol) in CH_2Cl_2 (0.5 mL). Purification through silica gel flash chromatography (5:1 to 3:1 hexanes-EtOAc) afforded a 2:1 mixture of products **38**:**39** (37 mg, 66%)**. Note:** Further purification of the mixture through silica gel flash chromatography (30:1 to 10:1 dichloromethane-EtOAc) can afford **38** or **39**. Data for **38**: **mp** 77-81°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.71-7.66 (m, 8H), 7.49-7.15 (m, 20H), 6.74-6.72 (m, 2H), 5.69 (d, *J* = 4.1 Hz, 1H), 5.51 (s, 1H), 5.18 (dd, *J* = 4.1, 9.8 Hz, 1H), 4.57-4.53 (m, 1H), 4.22 (t, *J* = 9.6 Hz, 1H), 4.08-4.00 (m, 3H), 3.95-3.90 (m, 2H), 3.83 (dd, *J* = 5.7, 10.4 Hz, 1H), 3.84 (d, *J* = 11.0 Hz, 1H), 3.64 (d, *J* = 10.7 Hz, 1H), 3.56 (t, *J* = 10.2 Hz, 1H), 3.54 (t, *J* = 9.5 Hz, 1H), 2.57 (br s, 1H), 2.43 (br s, 2H), 1.08 (s, 9H), 1.07 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 194.2, 153.1, 136.7, 135.7, 135.6, 135.5, 135.5, 132.9, 132.9, 132.8, 132.2, 129.9, 129.9, 129.8, 129.4, 129.3, 128.4, 127.9, 127.9, 127.8, 127.8, 126.4, 126.3, 121.7, 105.3, 102.1, 88.9, 81.1, 80.8,

80.8, 68.4, 68.3, 65.3, 63.2, 63.0, 26.9, 26.7, 19.2, 19.2; **IR** (film, cm^{-1}) 3448, 2925, 2851, 1275, 1213, 1111, 1070, 1013, 698, 662; **TLC** R_f 0.20 (20:1 dichloromethane-EtOAc); $[\alpha]_D^{20.0}$ +25.4 (*c* 0.70, $CHCl_3$); **HRMS** calcd for $[C_{58}H_{66}O_{12}Si_2S\ Na]^+$ requires *m/z* 1065.3711; found 1065.3711 (ESI+).

4,6-*O*-benzylidene-1´,6´-bis-*O*- t-butyldiphenylsilyl 3´-mono(thiocarbonate) sucrose 39.



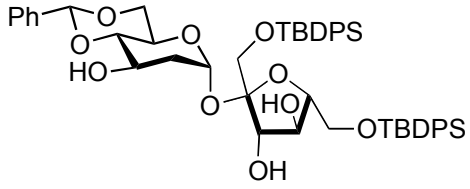
39

Data for **39**: **mp** 62-66°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.74-7.71 (m, 8H), 7.46-7.29 (m, 20H), 7.20-7.19 (m, 2H), 6.04 (d, *J* = 6.3 Hz, 1H), 5.67 (d, *J* = 4.1 Hz, 1H), 5.49 (s, 1H), 4.78 (dd, *J* = 6.1, 11.8 Hz, 1H), 4.18 (dd, *J* = 4.7, 10.1 Hz, 1H), 4.07 (dt, *J* = 5.0, 9.8 Hz, 1H), 4.03-3.97 (m, 2H), 3.88 (d, *J* = 11.0 Hz, 1H), 3.87 (d, *J* = 10.7 Hz, 1H), 3.82 (t, *J* = 9.5 Hz, 1H), 3.79 (d, *J* = 11.0 Hz, 1H), 3.57 (t, *J* = 10.2 Hz, 1H), 3.45-3.40 (m, 1H), 3.43 (t, *J* = 9.5 Hz, 1H), 2.65 (d, *J* = 5.4 Hz, 1H), 2.57 (br s, 1H), 2.24 (d, *J* = 10.1 Hz, 1H), 1.10 (s, 9H), 1.09 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.1, 153.4, 137.2, 135.8, 135.7, 135.6, 135.5, 132.8, 132.7, 132.4, 132.3, 130.0, 130.0, 129.9, 129.5, 129.0, 128.1, 127.9, 127.9, 127.8, 126.8, 126.4, 121.9, 104.4, 101.7, 91.8, 86.1, 82.3, 80.6, 73.7, 72.5, 71.9, 68.7, 66.9, 63.4, 62.6, 26.8, 26.8, 19.3, 19.2; **IR** (film, cm^{-1}) 3440, 2929, 2856, 1283, 1201, 1111, 1070, 739, 698; **TLC** R_f 0.50 (20:1 dichloromethane-EtOAc); $[\alpha]_D^{20.0}$ -3.20 (*c* 1.0, $CHCl_3$); **HRMS** calcd for $[C_{58}H_{66}O_{12}Si_2S\ Na]^+$ requires *m/z* 1065.3711; found 1065.3740 (ESI+).

2.3 General Procedure for the Deoxygenation Reaction.

To a solution of the corresponding mono or bis thiocarbonate (1 equiv) in toluene (4 mL), tributyltin hydride (3 equiv) and AIBN (0.3 equiv) were added and the mixture was heated at reflux for 3 h. Solvent was then removed under reduced pressure and the resulting residue was purified by silica gel flash chromatography (3:1 to 2:1, hexanes-EtOAc).

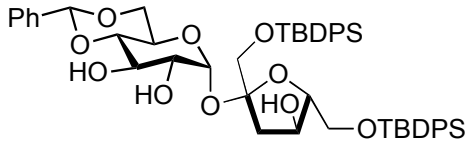
Compound 40.



40

General procedure for deoxygenation was followed, sucrose derivative **38** (25 mg, 0.024 mmol) was employed as starting material with AIBN (1.2 mg, 0.007 mmol) and tributyltin hydride (19 μL, 0.072 mmol). Compound **40** was isolated as a clear oil (10 mg, 48%). Data for **40**: **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.71-7.66 (m, 8H), 7.46-7.35 (m, 17H), 5.66 (d, *J* = 3.3 Hz, 1H), 5.52 (s, 1H), 4.41 (dd, *J* = 8.2 Hz, *J* = 10.5 Hz, 1H), 4.23 (dd, *J* = 8.2 Hz, *J* = 3.7 Hz, 1H), 4.10-4.01 (m, 2H), 3.97-3.83 (m, 3H), 3.74 (d, *J* = 10.6 Hz, 1H), 3.64-3.58 (m, 2H), 3.34 (t, *J* = 9.2 Hz, 1H), 3.02 (d, *J* = 10.9 Hz, 1H), 2.35 (d, *J* = 2.5 Hz, 1H), 2.27 (d, *J* = 3.8 Hz, 1H), 1.96 (dd, *J* = 5.1 Hz, *J* = 13.9 Hz, 1H), 1.67-1.46 (m, 2H), 1.09 (s, 9H), 1.06 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 137.1, 135.6, 135.6, 135.5, 135.5, 133.1, 132.8, 132.8, 132.8, 130.0, 129.9, 129.8, 129.8, 129.3, 128.3, 127.9, 127.8, 127.7, 126.3, 105.2, 102.0, 91.1, 83.4, 80.4, 77.7, 75.9, 68.6, 65.4, 65.4, 63.8, 63.4, 37.8, 26.9, 26.8, 19.3, 19.2; **IR** (film, cm^{-1}) 3440, 2934, 2852, 1434, 1115, 1017, 821, 743, 707; **TLC** R_f 0.20 (2:1 hexanes-EtOAc); **[α]** $^{20.0}_{D}$ +8.8 (*c* 0.27, $CHCl_3$); **HRMS** calcd for $[C_{51}H_{62}O_{10}Si_2\ Na]^+$ requires *m/z* 913.3779; found 913.3733 (ESI+).

Compound 41.



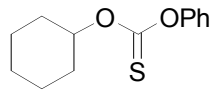
41

General procedure for deoxygenation was followed, sucrose derivative **39** (23 mg, 0.022 mmol) was employed as starting material with AIBN (1.0 mg, 0.007 mmol) and tributyltin hydride (17.5 μL, 0.066 mmol). Compound **41** was isolated as a clear oil (8.0 mg, 42%). Data for **41**: **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.72-7.65 (m, 8H), 7.50-7.35 (m, 17H), 5.48 (s, 1H), 5.39 (d, *J* = 4.1 Hz, 1H), 5.44-5.42 (m, 1H), 4.23-4.20 (m, 1H), 3.99-3.92 (m, 3H), 3.84-3.79 (m, 2H), 3.71 (d, *J* = 10.7 Hz, 1H); 3.61 (d, *J* = 10.7 Hz, 1H), 3.53 (t, *J* = 10.4 Hz, 1H), 3.44 (dd, *J* = 3.8 Hz, *J* = 9.1 Hz, 1H), 3.40 (t, *J* = 9.5 Hz, 1H), 2.42 (dd, *J* = 6.9 Hz, *J* = 13.9

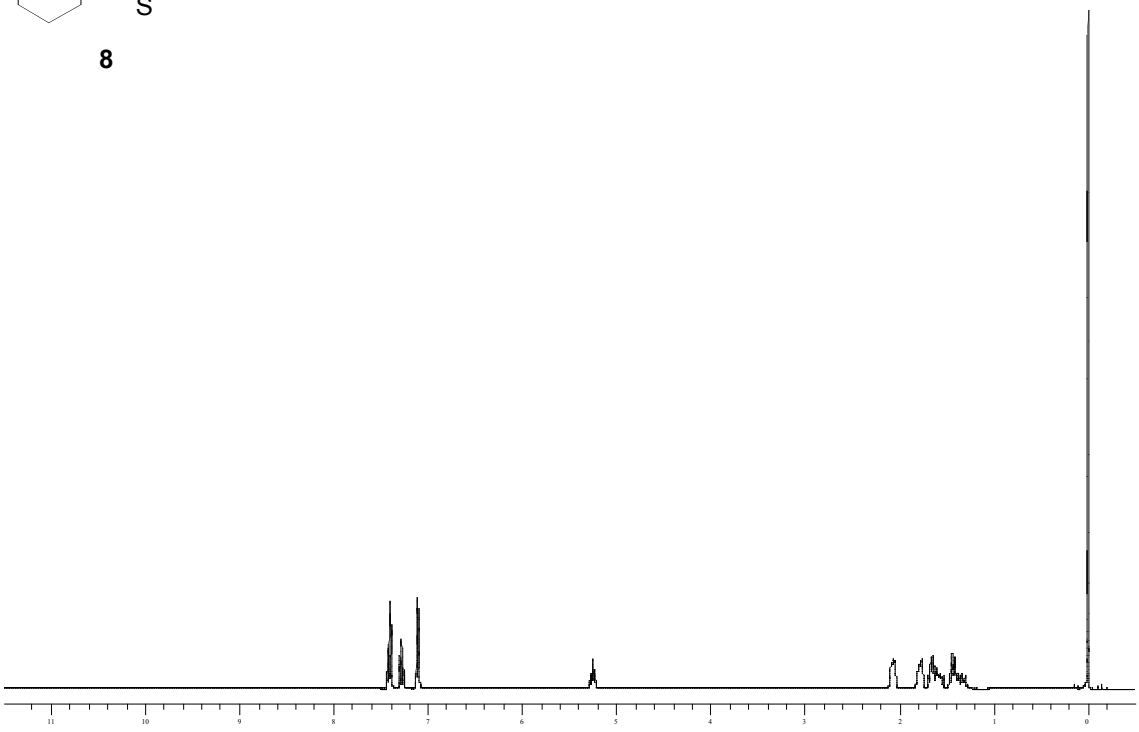
Hz, 1H), 2.33 (br s, 3H), 2.06 (dd, J = 5.7 Hz, J = 13.9 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 135.8, 135.6, 135.6, 135.5, 132.4, 132.3, 130.9, 130.1, 130.1, 129.9, 129.9, 129.3, 128.8, 128.3, 127.9, 127.9, 127.8, 126.3, 124.1, 121.0, 108.8, 101.8, 92.2, 86.8, 80.8, 72.5, 71.8, 68.7, 66.8, 66.2, 65.9, 64.2, 63.0, 38.8, 26.9, 19.2, 19.2; **IR** (film, cm^{-1}) 3375, 2958, 2952, 2852, 1728, 1283, 1119, 1074, 698; **TLC** R_f 0.20 (2:1 hexanes-EtOAc); $[\alpha]_D^{20.0}$ +9.9 (*c* 0.22, $CHCl_3$); **HRMS** calcd for $[C_{51}H_{62}O_{10}Si_2\ Na]^+$ requires *m/z* 913.3779; found 913.3795 (ESI+).

NMR Spectra

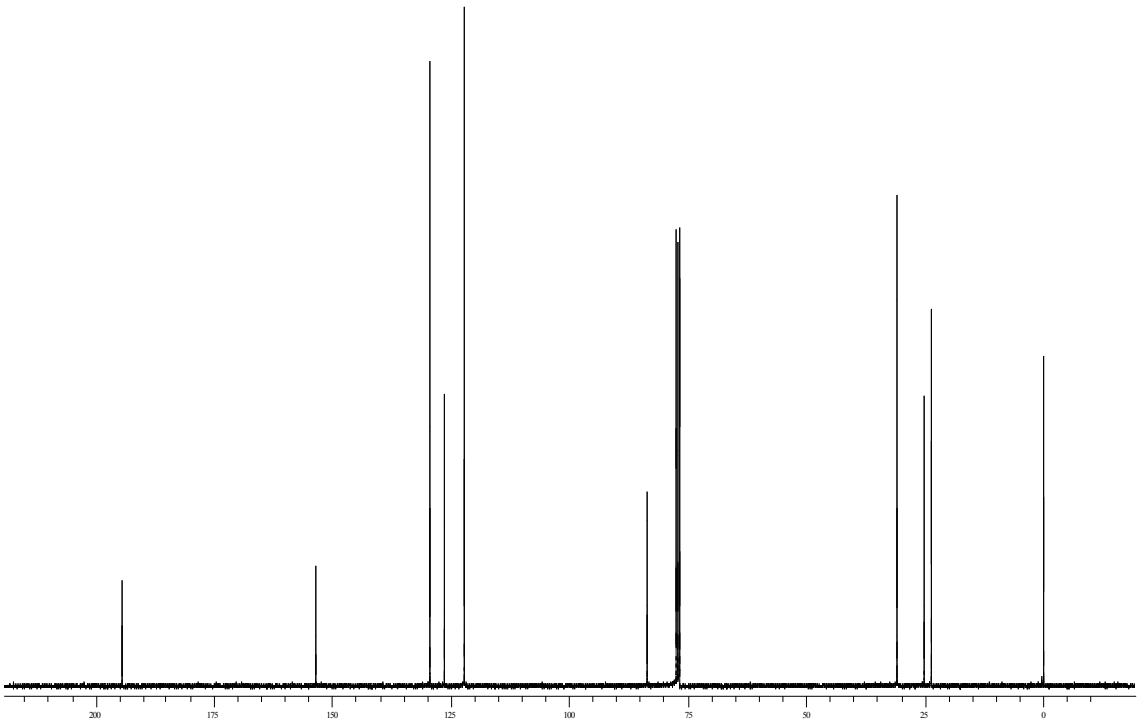
^{1}H NMR Spectrum of Compound 8.



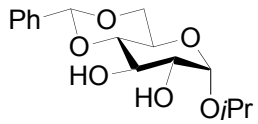
8



^{13}C Spectrum of Compound 8.

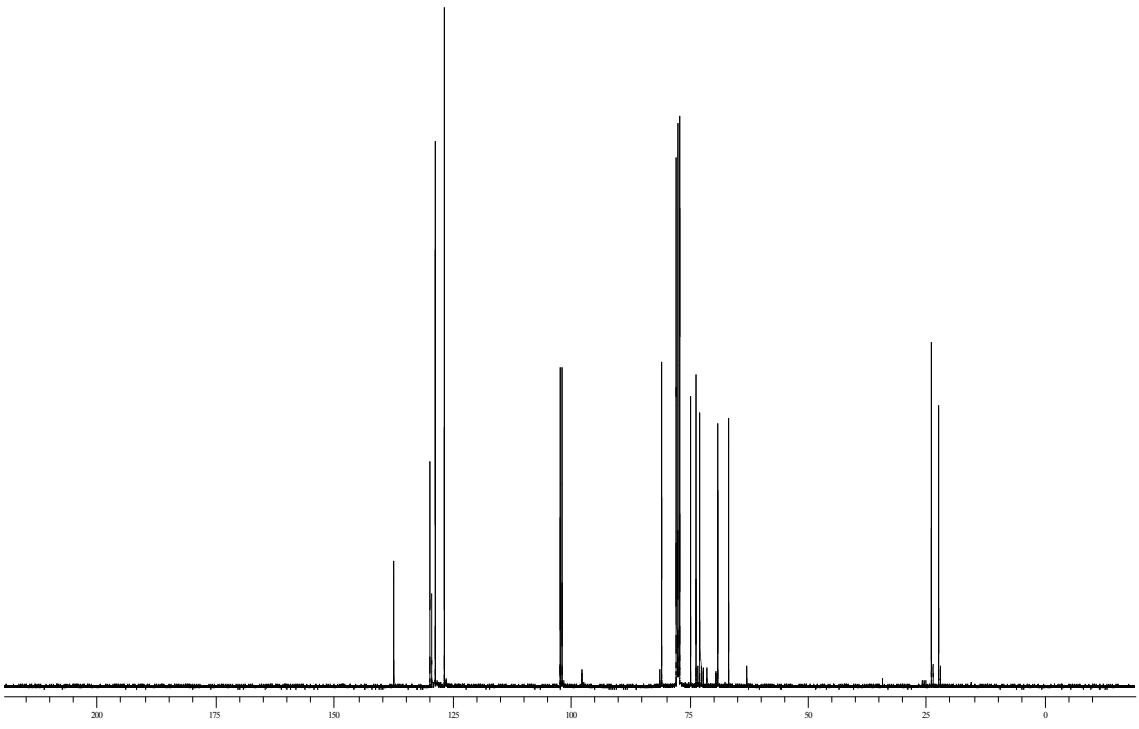


^{1}H NMR Spectrum of Compound 12b.

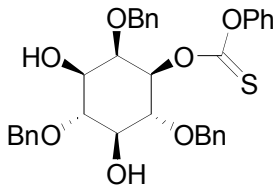


12b

^{13}C NMR Spectrum of Compound 12b.

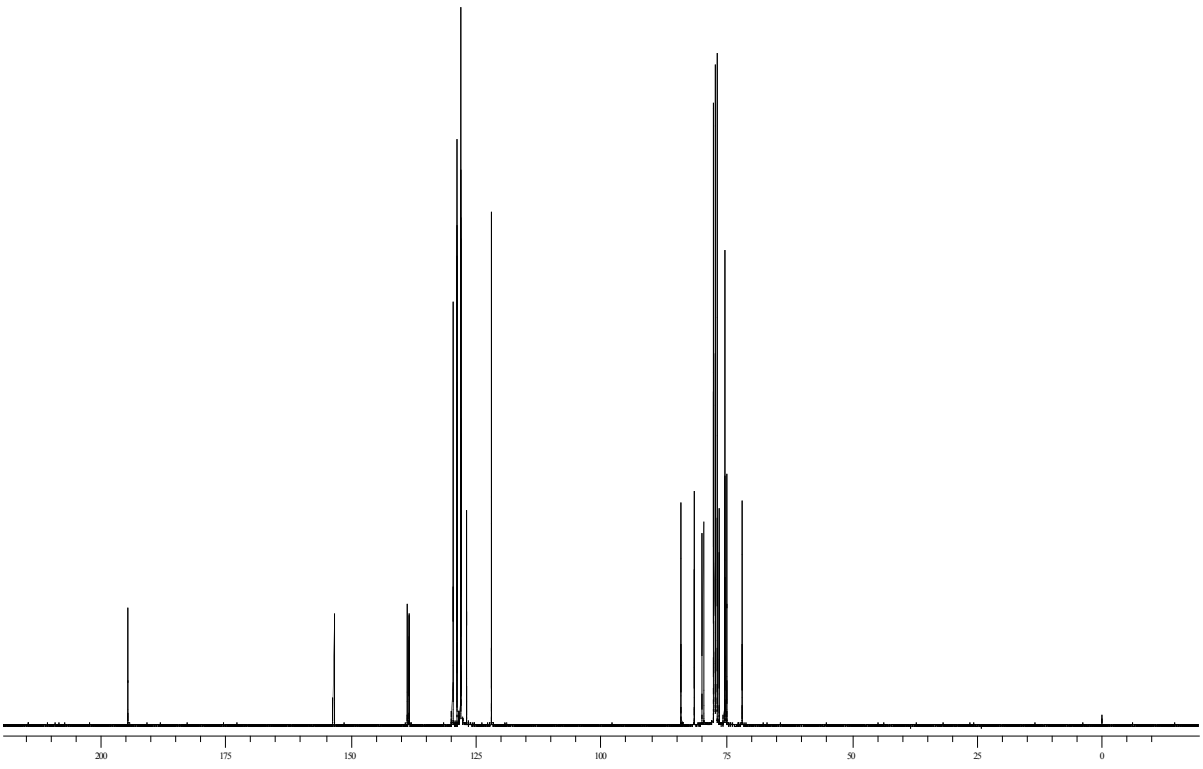


^{1}H NMR Spectrum of Compound (±)-13.

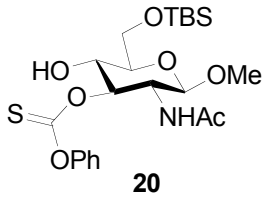


(±)-**13**

^{13}C Spectrum of Compound (±)-13.

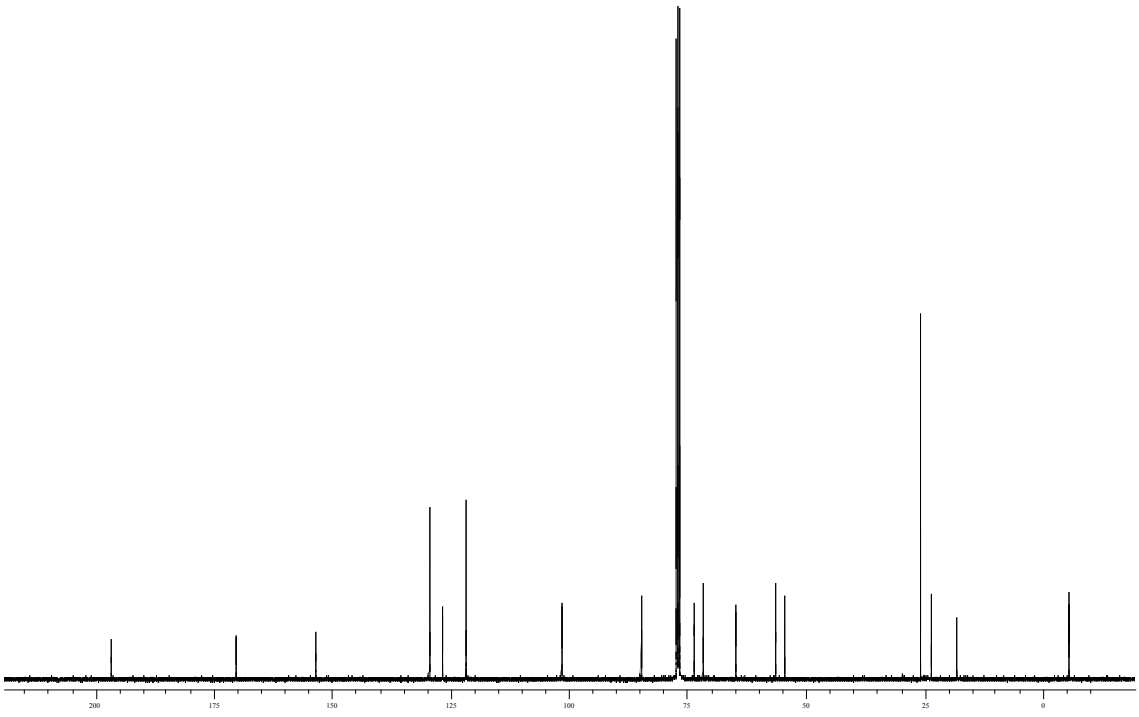


^{1}H NMR Spectrum of Compound 20.

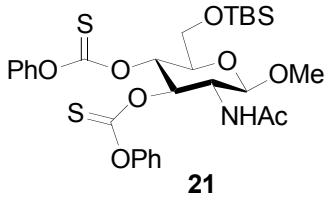


20

^{13}C NMR Spectrum of Compound 20.

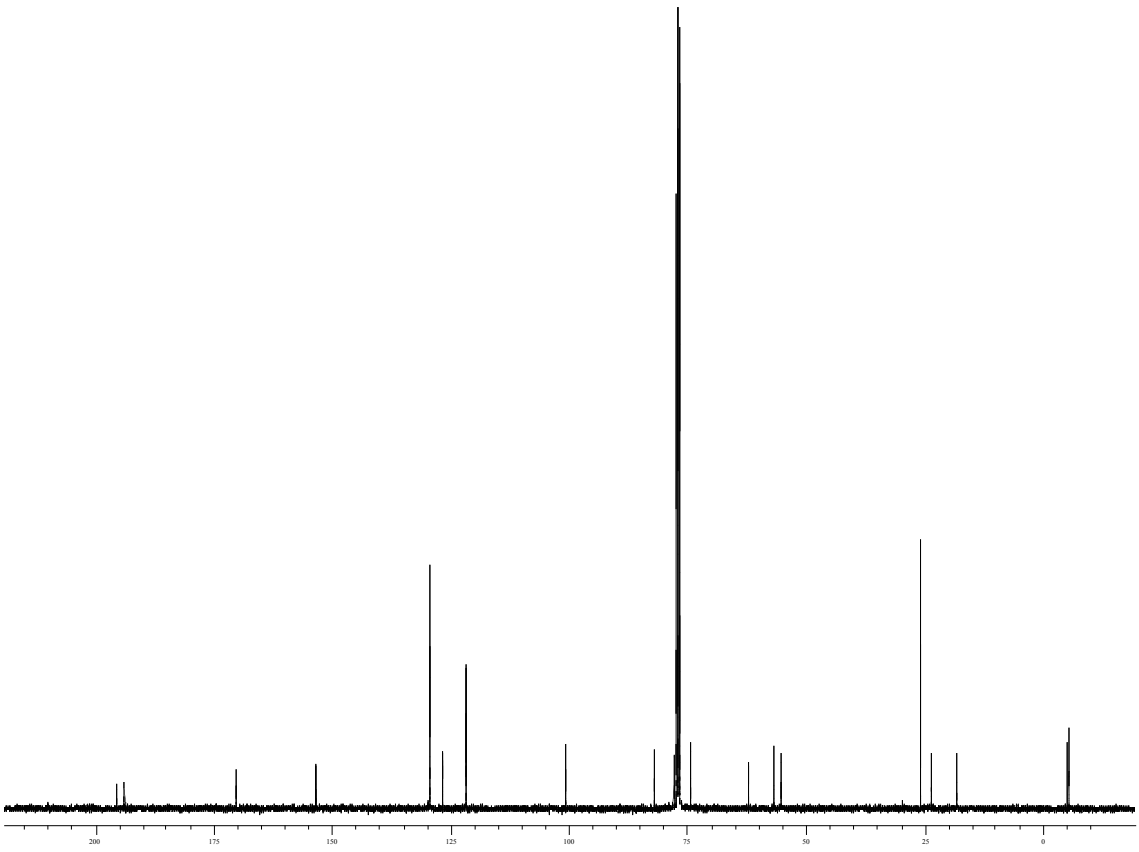


[1]H NMR Spectrum of Compound 21.

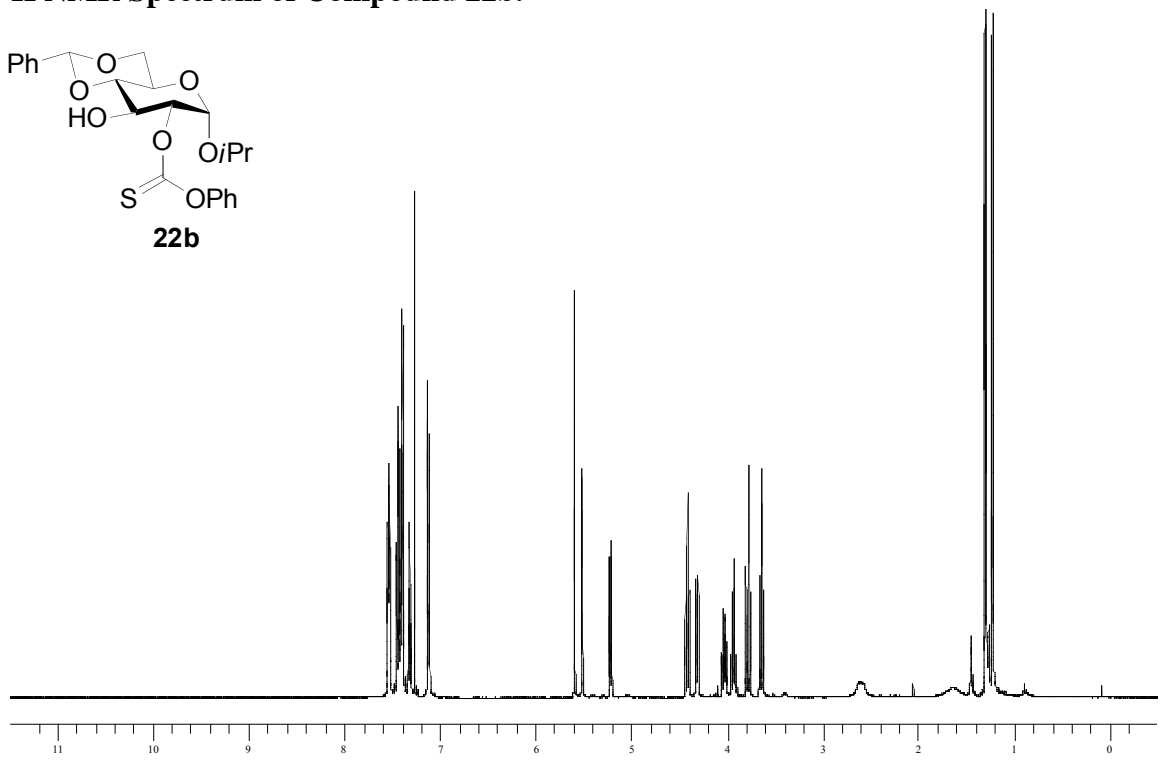


21

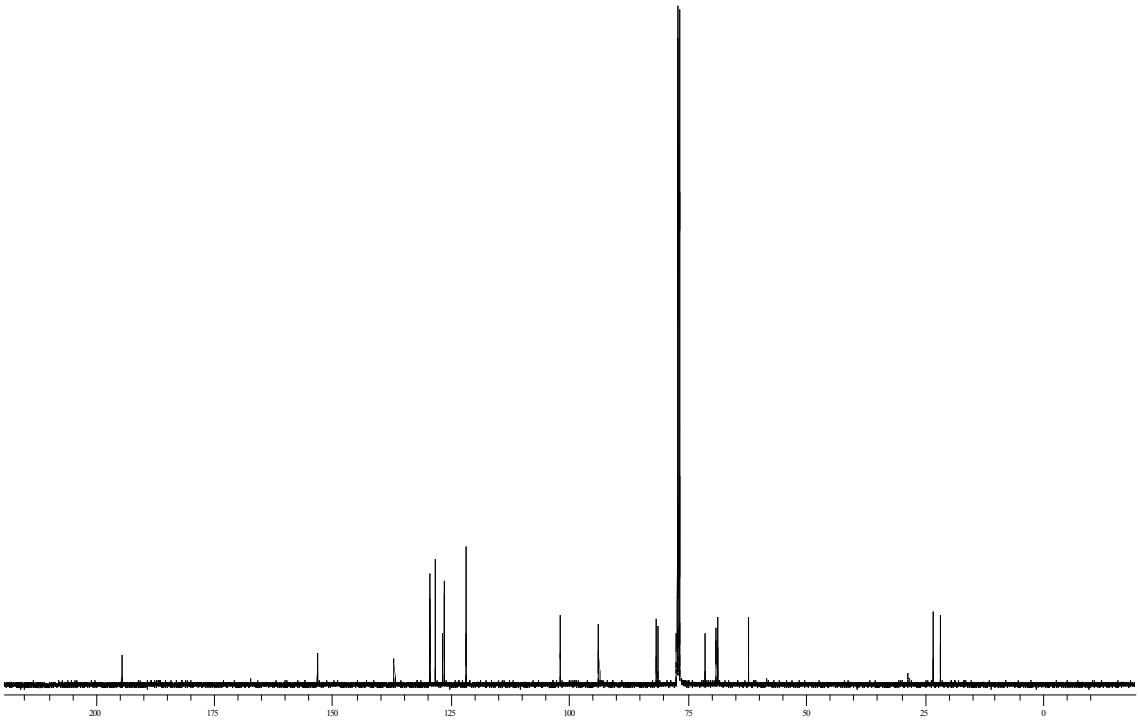
[13]C Spectrum of Compound 21.



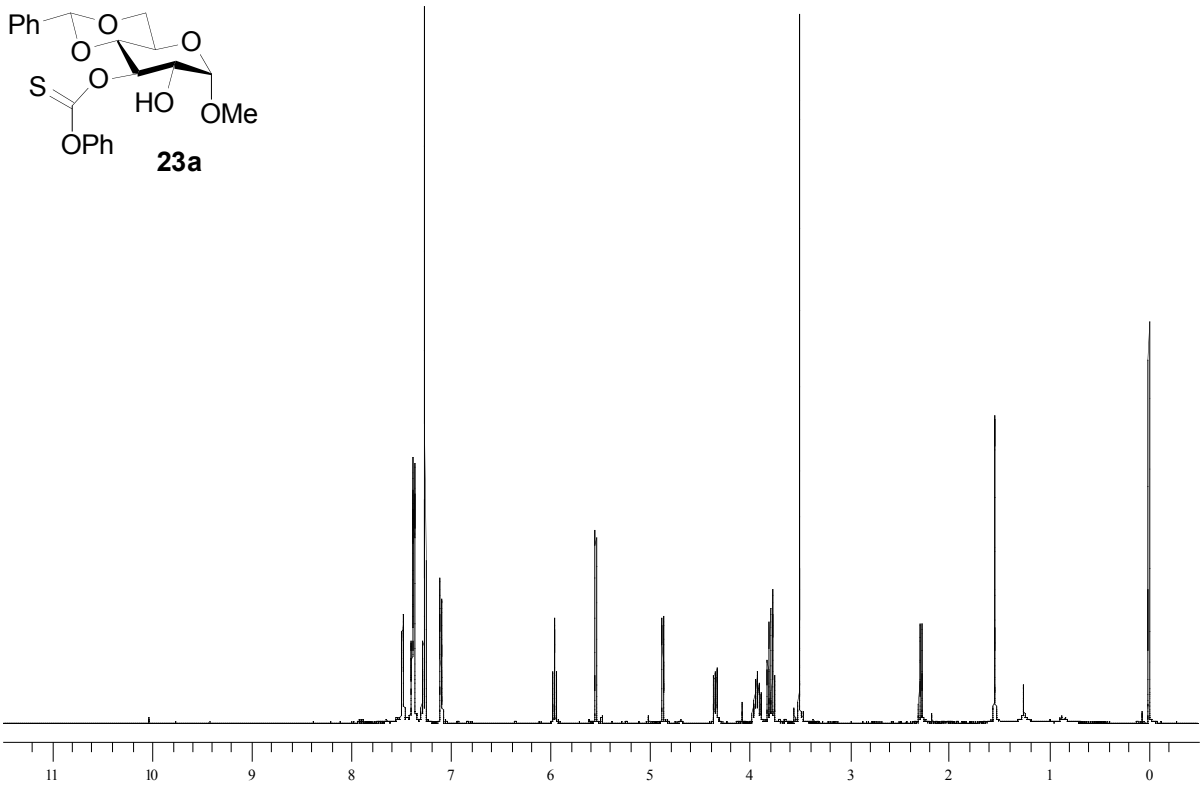
^{1}H NMR Spectrum of Compound 22b.



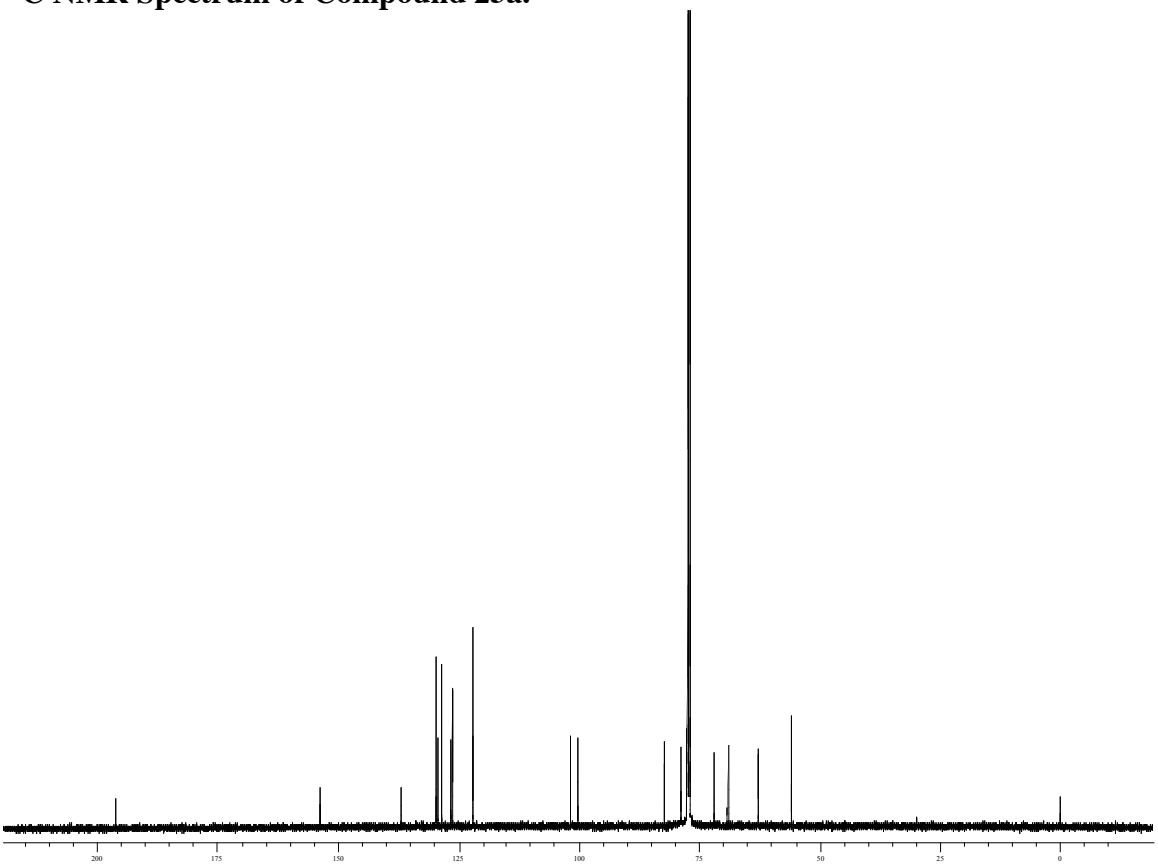
^{13}C NMR Spectrum of Compound 22b.



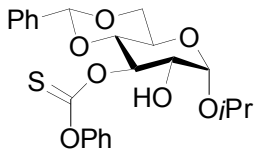
^{1}H NMR Spectrum of Compound 23a.



^{13}C NMR Spectrum of Compound 23a.

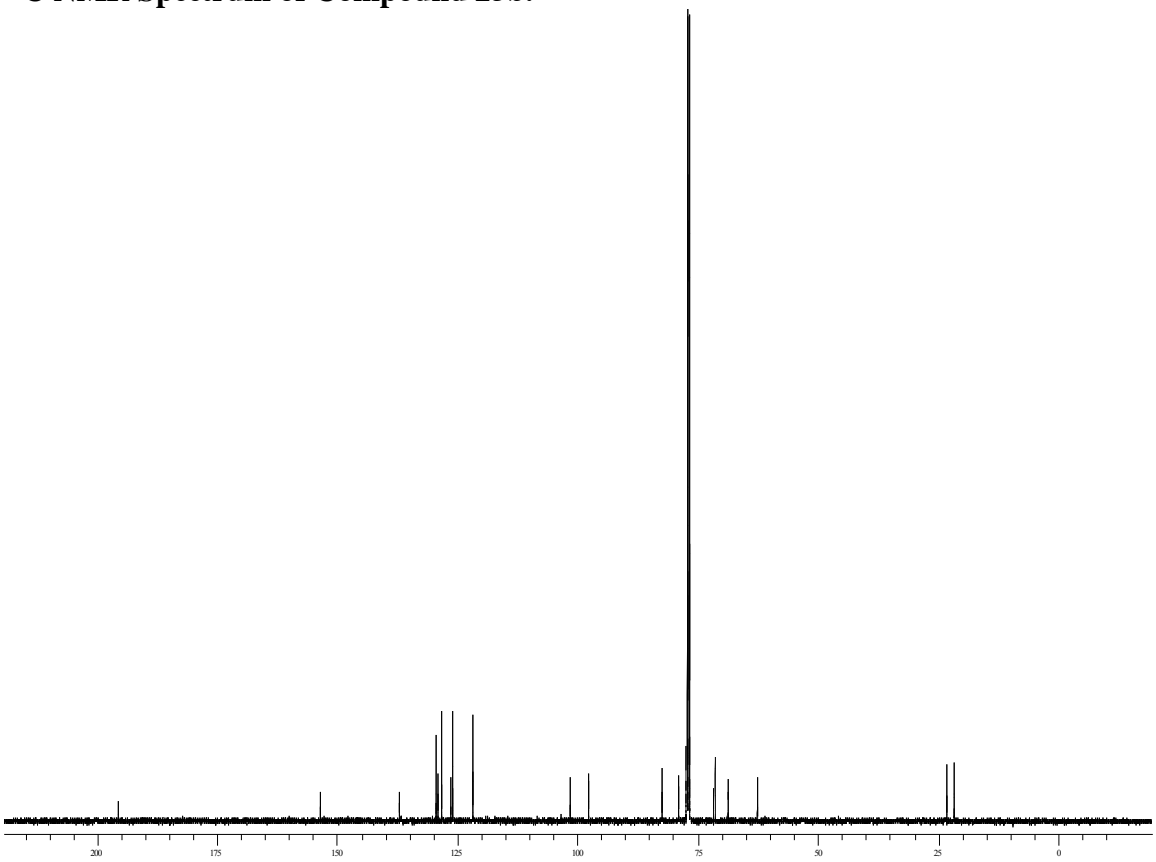


^{1}H NMR Spectrum of Compound 23b.

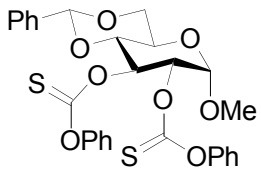


23b

^{13}C NMR Spectrum of Compound 23b.

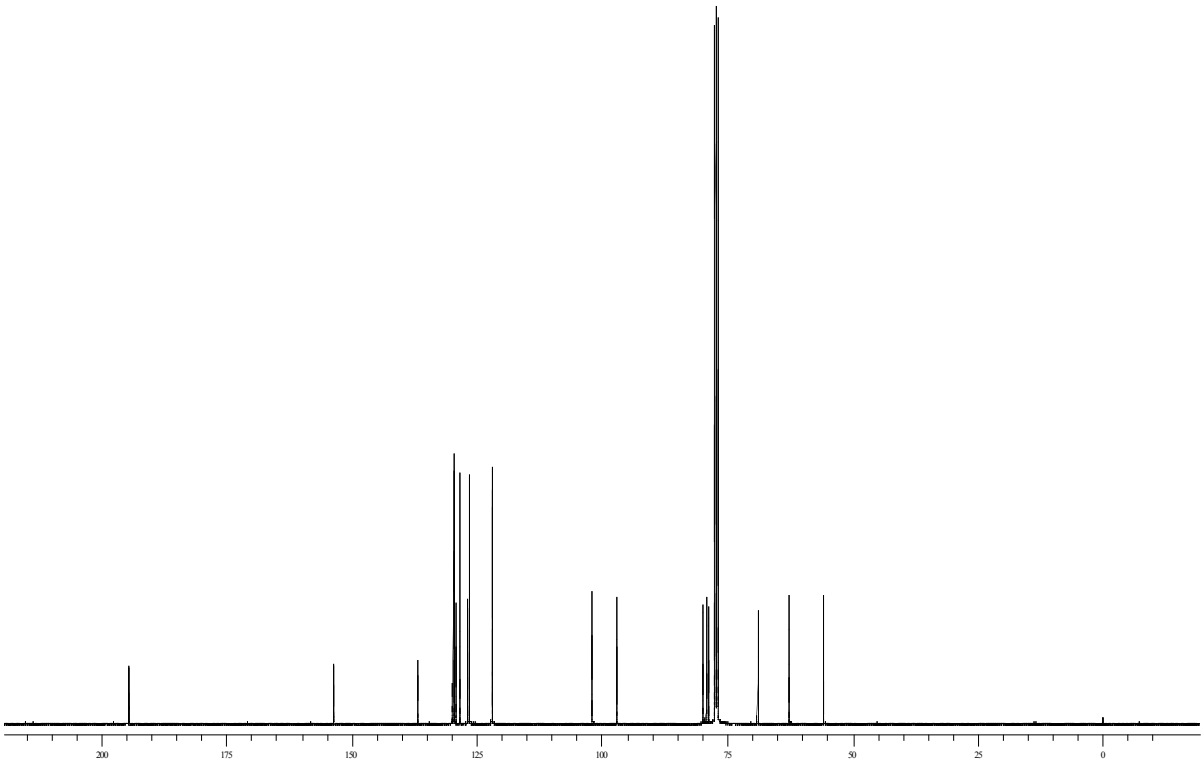


^{1}H NMR Spectrum of Compound 24a.

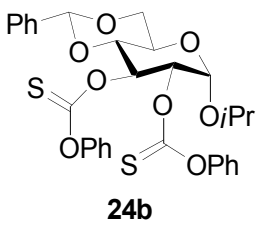


24a

^{13}C NMR Spectrum of Compound 24a.

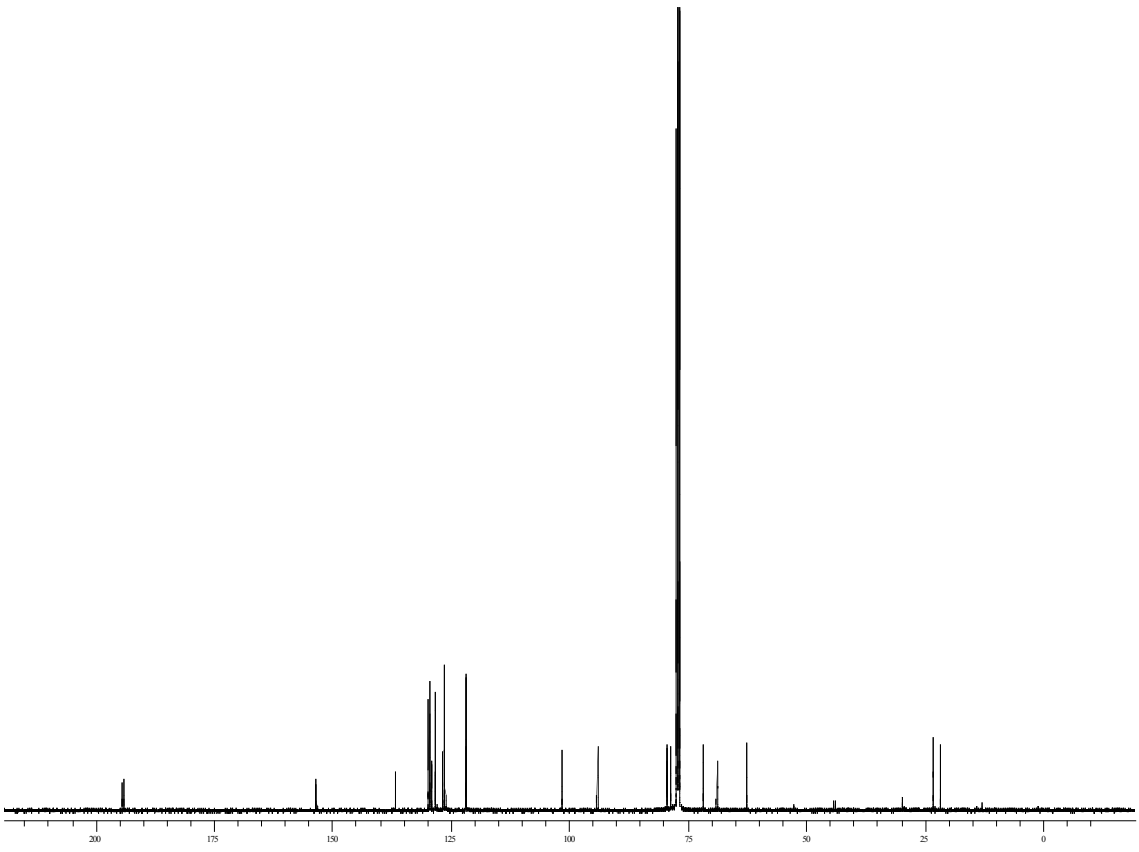


^{1}H NMR Spectrum of Compound 24b.

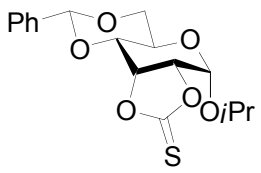


24b

^{13}C NMR Spectrum of Compound 24b.

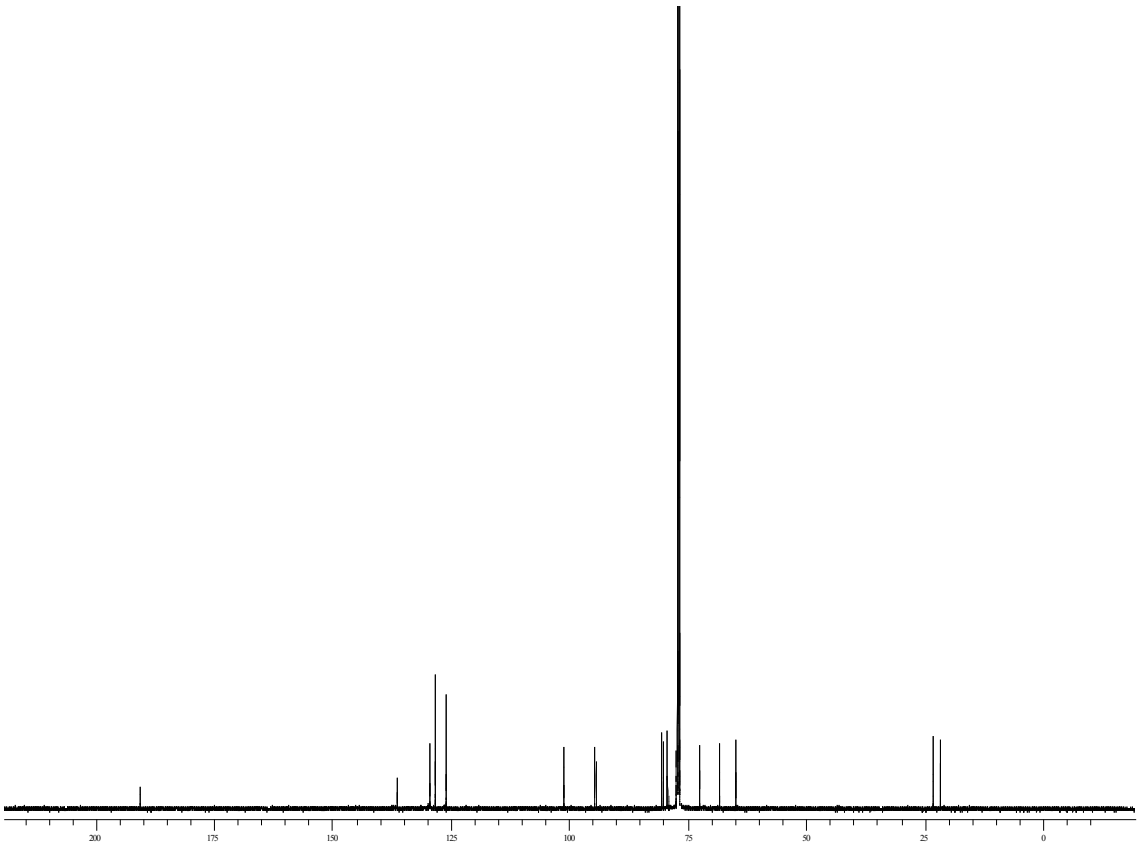


^{1}H NMR Spectrum of Compound 26b.

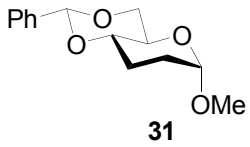


26b

^{13}C NMR Spectrum of Compound 26b.

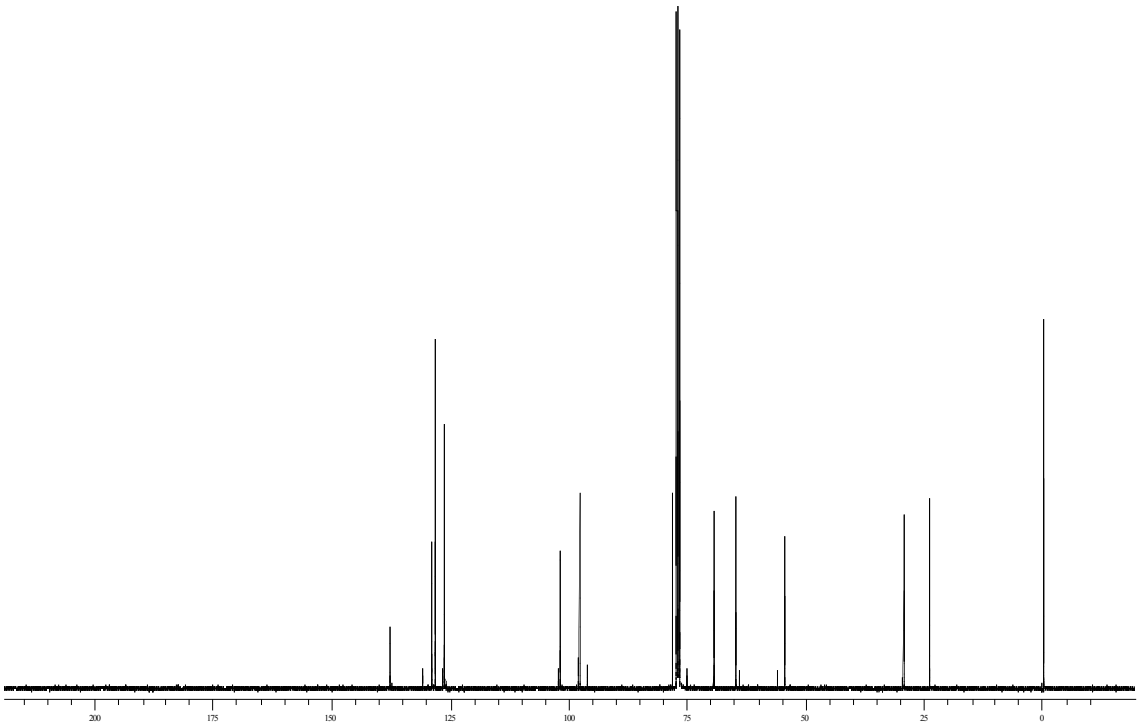


^{1}H NMR Spectrum of Compound 31.

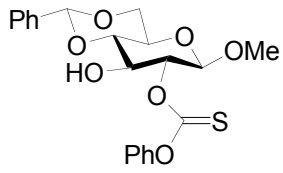


31

^{13}C NMR Spectrum of Compound 31.

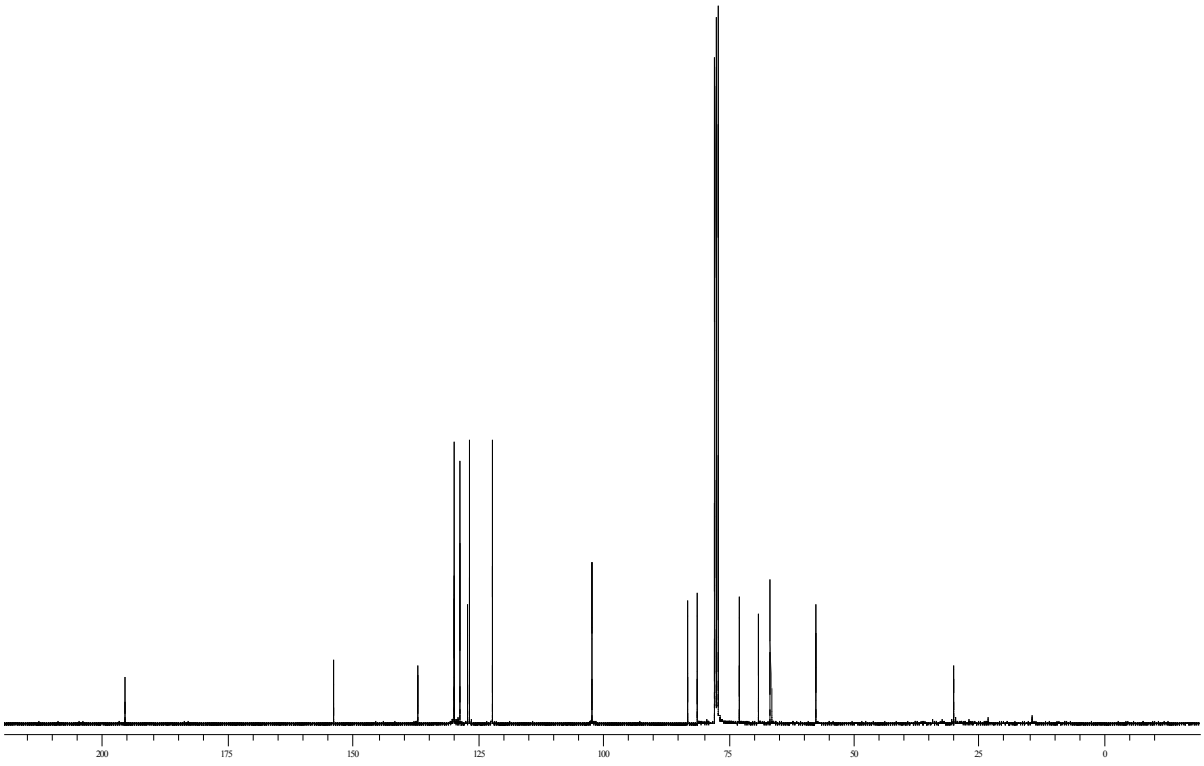


^{1}H NMR Spectrum of Compound 33.

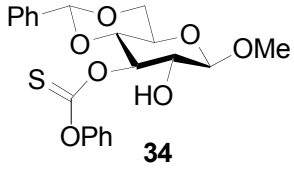


33

^{13}C NMR Spectrum of Compound 33.

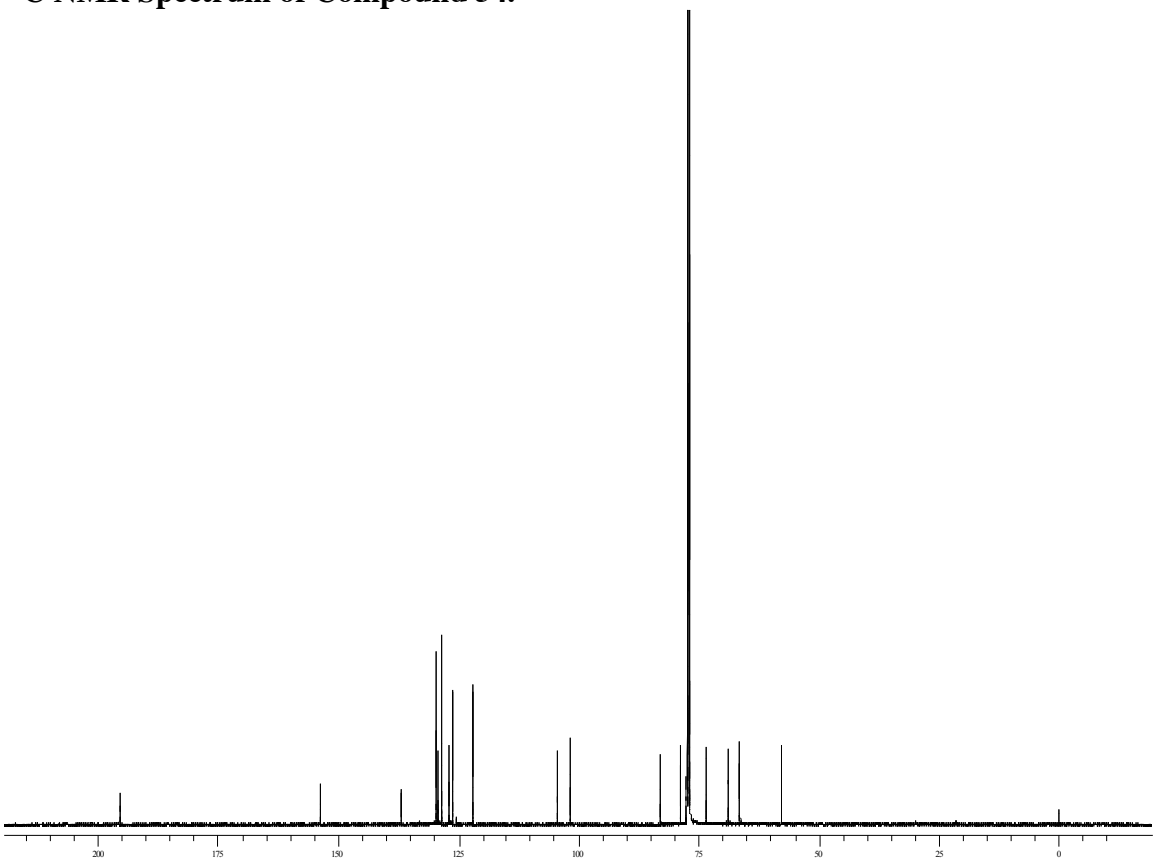


^{1}H NMR Spectrum of Compound 34.

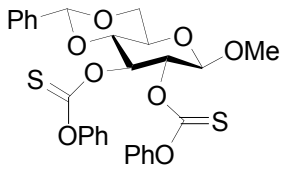


34

^{13}C NMR Spectrum of Compound 34.

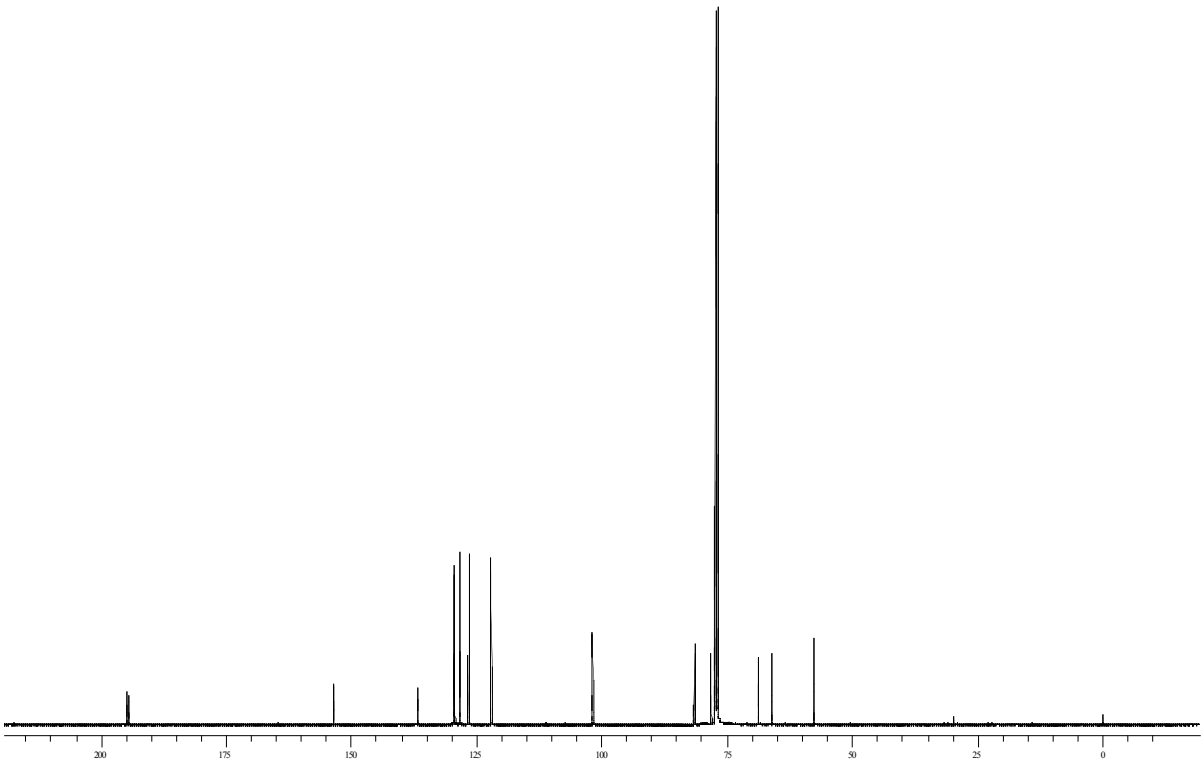


^{1}H NMR Spectrum of Compound 35.

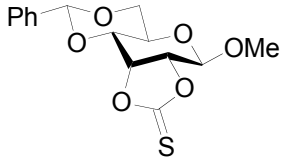


35

^{13}C NMR Spectrum of Compound 35.

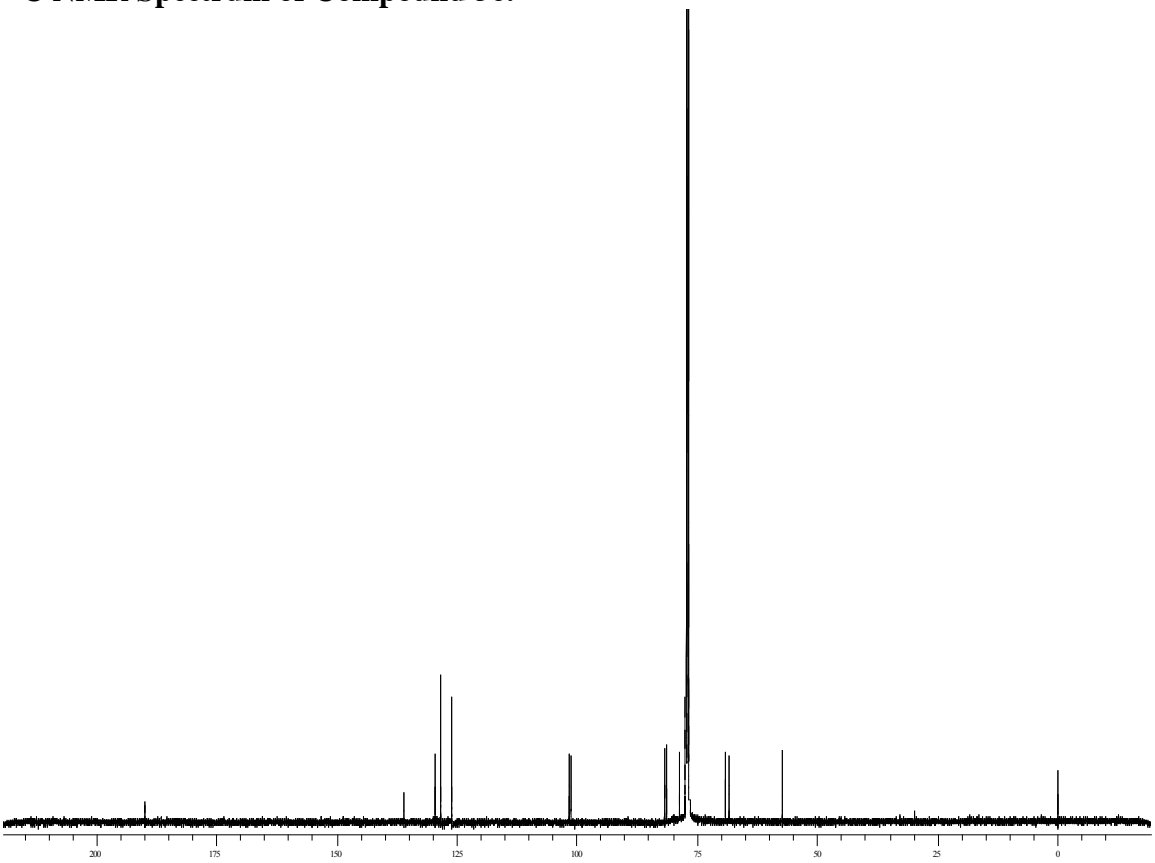


^{1}H NMR Spectrum of Compound 36.

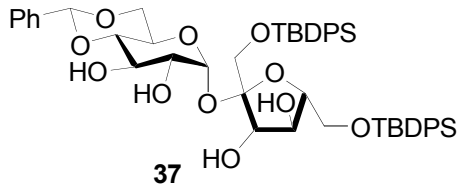


36

^{13}C NMR Spectrum of Compound 36.

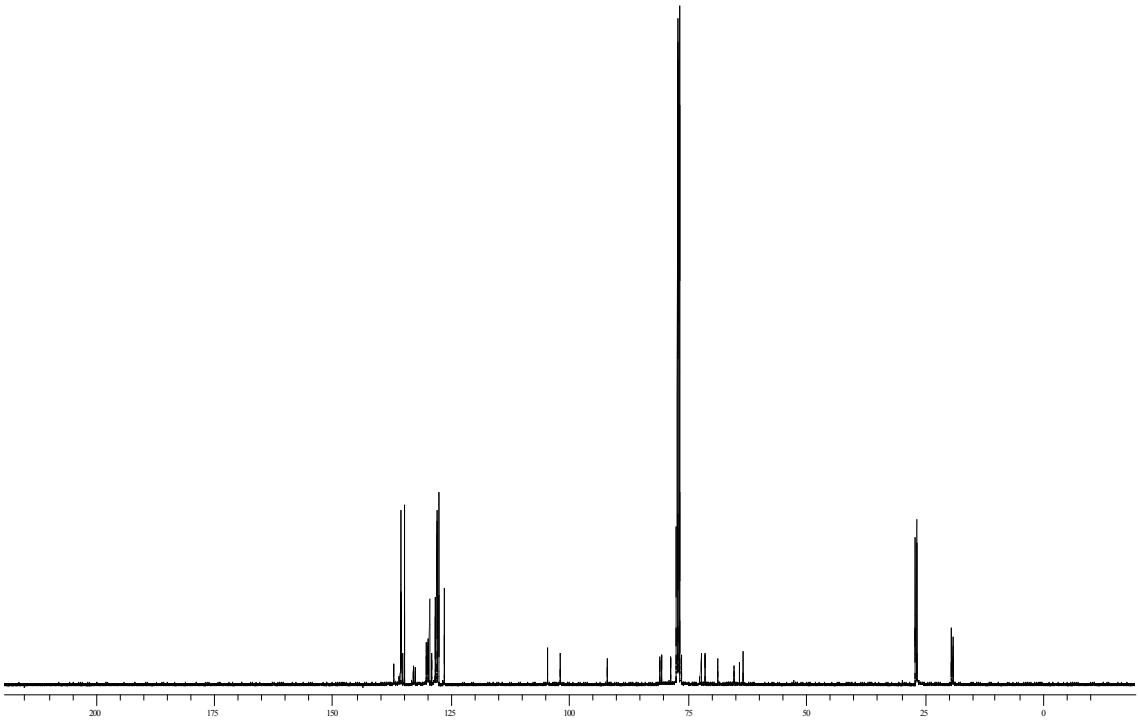


[1]H NMR Spectrum of Compound 37.

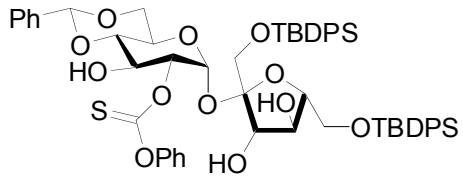


37

[13]C NMR Spectrum of Compound 37.

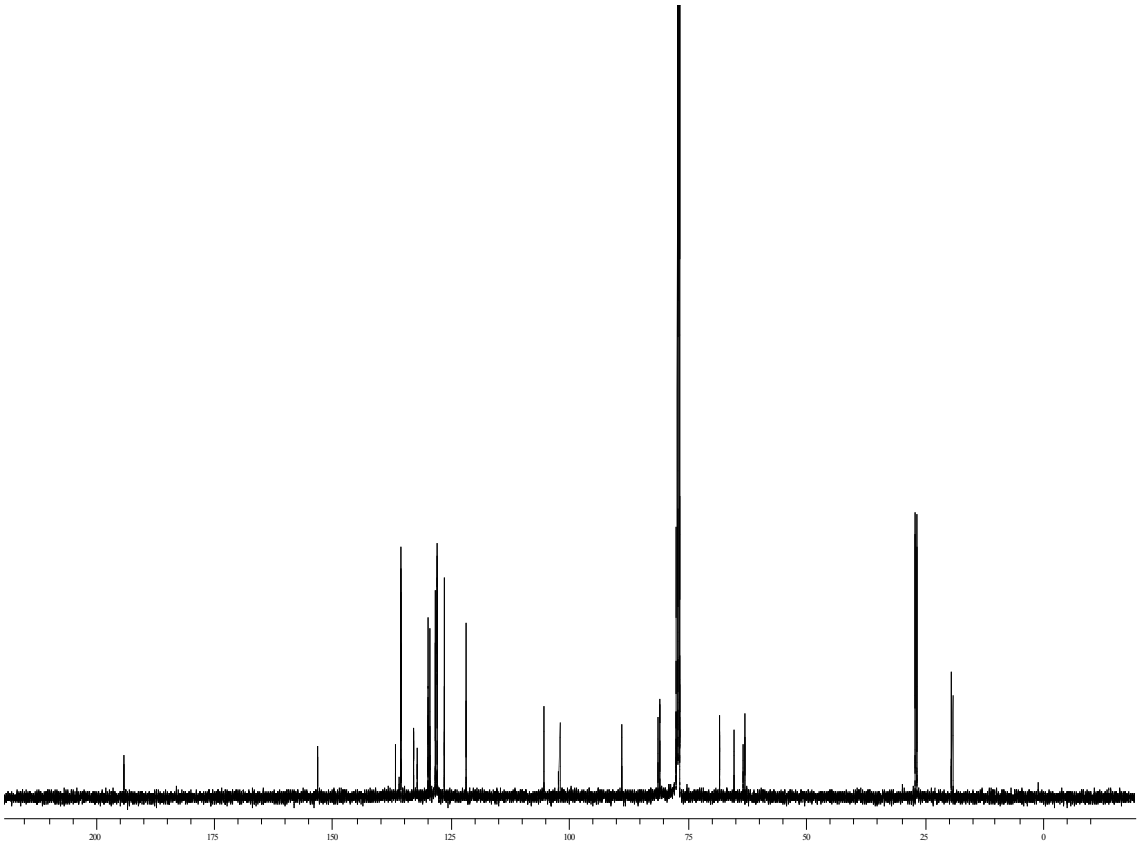


^{1}H NMR Spectrum of Compound 38.

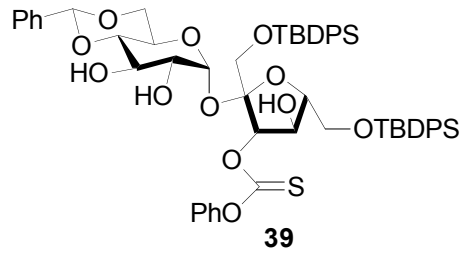


38

^{13}C NMR Spectrum of Compound 38.

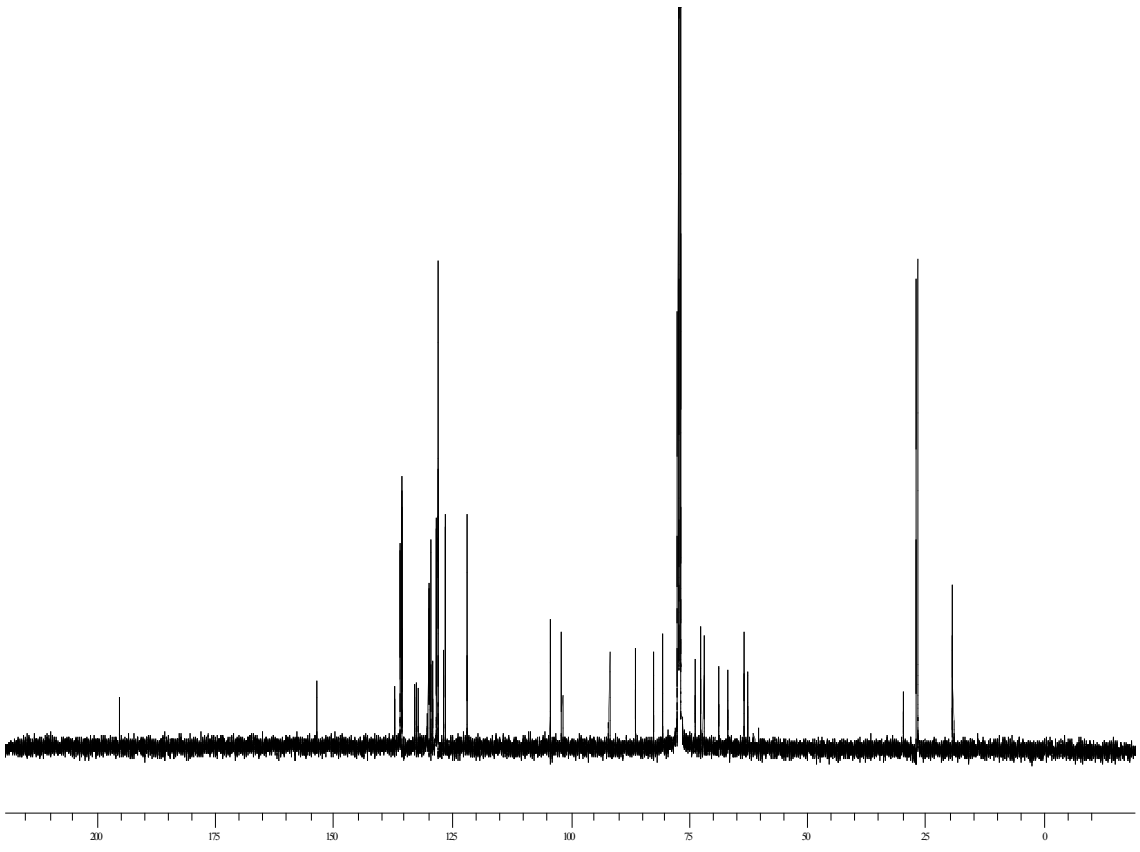


[1]H NMR Spectrum of Compound 39.

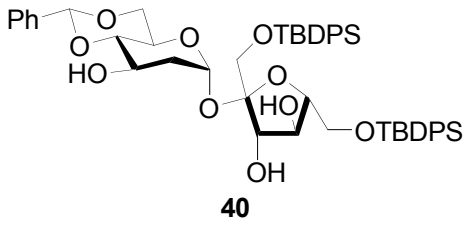


39

[13]C NMR Spectrum of Compound 39.

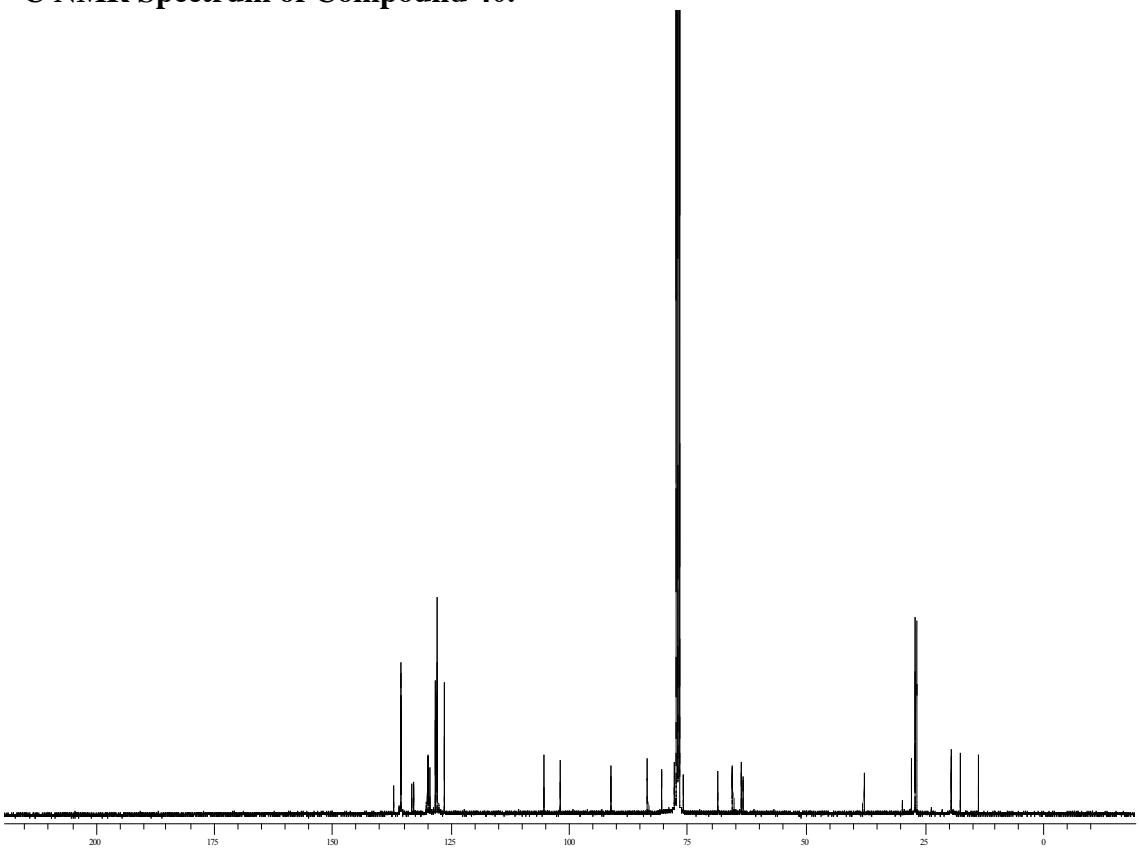


^{1}H NMR Spectrum of Compound 40.

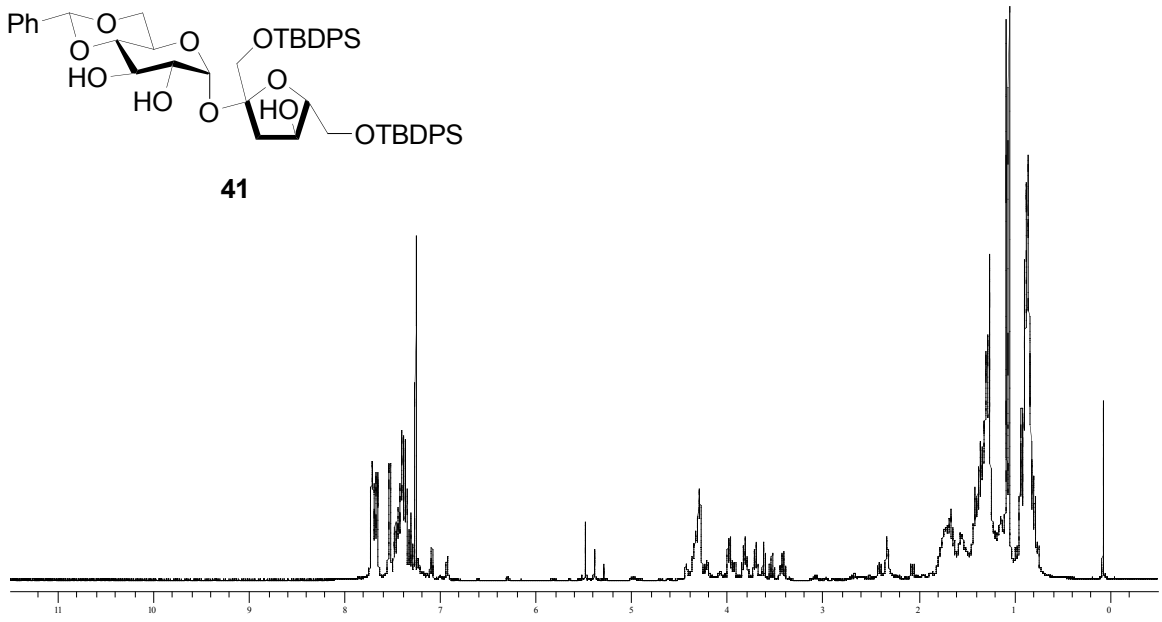


40

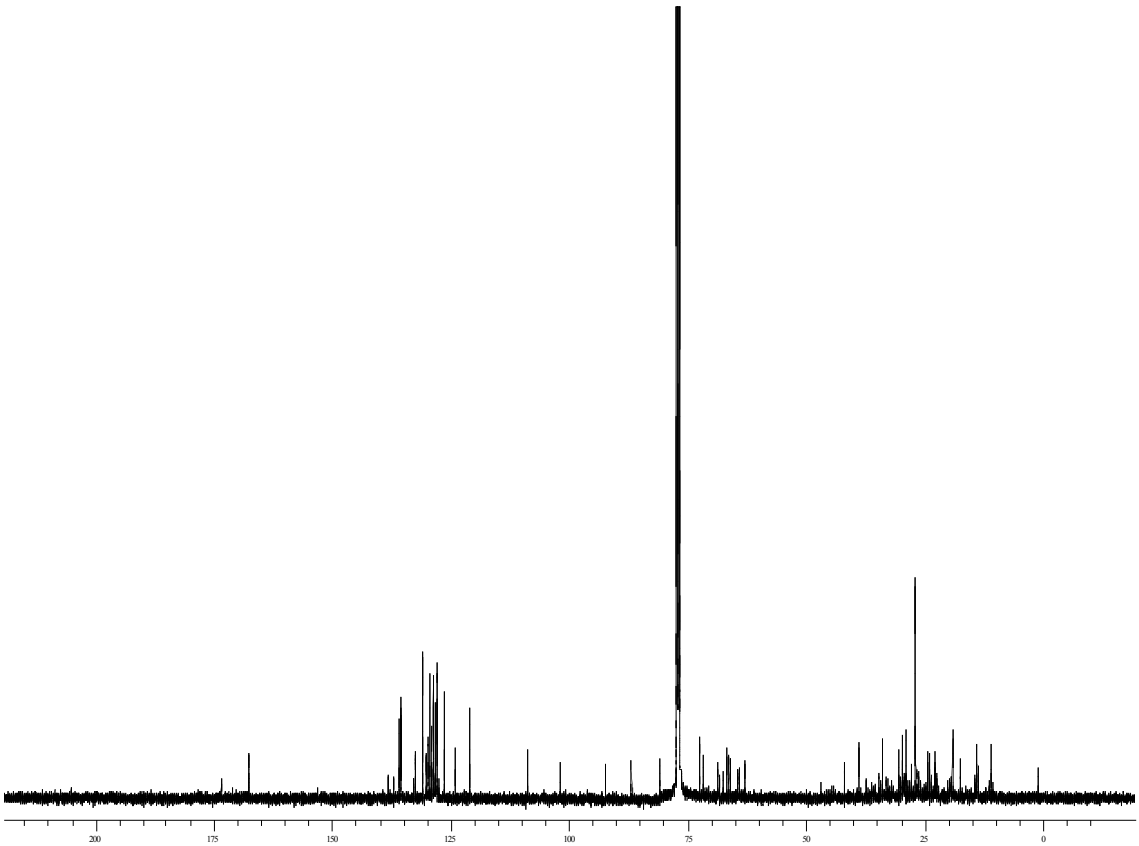
^{13}C NMR Spectrum of Compound 40.



^{1}H NMR Spectrum of Compound 41.



^{13}C NMR Spectrum of Compound 41.



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